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SPECTROSCOPIC CONFERENCE

WITH INTERNATIONAL PARTICIPATION

ABSTRACTS

ČESKÉ BUDĚJOVICE

June 22. - 24.1992

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In this volume the abstracts are ordered alphabetically according to the first author of the contribution and are coded to the sections as follows :

A - atomic spectroscopy
F - instrument manufacturer
M - molecular spectroscopy
S - special spectroscopy methods

A 1

SELENIUM AND CARDIOVASCULAR DISEASE IN ELDERLY PEOPLE

D. Adamečková, J. Gratzlová, L. Hegyi
Research Institute of Gerontology, Malacky

The serum selenium content was determined by flameless AAS in the case of patients with cardiovascular disease in age 56-89 year and it was compared with control group of the same age. Control group was presented by 20 relativly healthy people aged 60 - 90 year (44,85 + 8,62 ng/ml). Examined group consisted of 35 patients with cardiovascular disease, 18 patients had infarct myocardu (34,28 + 12,04 ng/ml), 8 had angina pectoris (44,15 + 7,24 ng/ml), 9 had ischemic heart disease (41,15 + 10,10 ng/ml). There were significant difference in serum selenium content between patients with infarct myocardu and control group of the same age ($p < 0,01$).

The results suggest that the decresed serum selenium in controled group and in the case of patients with infarct myocardu can by one of the risk factor for this disease.

THE EFFECT OF COMPLEXING AGENTS ON COPRECIPITATION OF URANIUM WITH IMPURITIES AND THEIR DETERMINATION WITH ICP-AES

S. Albayrak, L. Güreli, R. Uzmen, İ. Yıldız
Çekmece Nuclear Research and Training Center
P.O. box 1 Havaalanı Istanbul TURKEY

ABSTRACT

Waste solutions from UO_2 production pilot plant have a which have a high content of uranium 5 g/l such as acidified extraction raffinate are treated with a complexing agent. One way of recovering uranium from these waste solutions is to precipitate as the ammonium diuranate compound. In order to prevent the coprecipitation of impurities with uranium, complexing agent ethylene diamine tetra acetic acid was added to the solutions and its effect on the impurities was studied. The pH on precipitation and the necessary amount of EDTA were determined. The impurities considered in this study were Al, Ba, Ca, Cr, Cu, Fe, Mg, Mn, Ni, and Zn because of their ease of complex formation with EDTA and also because they have high initial concentrations. The decontamination factors for these elements were determined. experiments were carried out on both simulated solutions and process solutions. Other chelating agents of the same type i.e. CDTA and DTPA were also tried.

It was found that addition of a complexing agent resulted in a higher purity uranium compound.

A 3

HEAVY METALS IN PEATS

J. Bastl, K. Drbal

Jihočeska Univerzita, Zemédélska fakulta, katedra chemie
České Budéjovice

Concentracion of ten heavy metals and of arsenic were determined using AAS method in peats from the South Bohemia during 1989. Samples were collected from eight sites of peateries in Třeboň Basin and from five sites in the Šumava Mountains. Some peatbogs are intact, the other are exploited. Following concentrations ($mg.kg^{-1}$) were found in the top layer of 20cm thickness: Cu 4.38 - 26.4; Mn 12.0 - 169.0; Fe 1410 - 12300; Zn 17.6 - 53.2; Co 1.07 - 10.6; Ni 3.68 - 24.9; Cr 2.03 - 14.2; Cd 0.11 - 1.06; Pb 2.03 - 67.6; Hg 0.091 - 0.417 and As 0.33 - 1.11.

Elevated concentratoins of Cu, Cr, Ni and Co were found in the peats from several sites of the Třeboň Basin, both intact and exploited. High Fe and Mn levels were determined in the exploited peatbogs of both the regions. On the contrary , higher mean concentrations of Pb, Cd and Hg were found in the intact peateries of both regions.

Changes of the elements concentrations were monitored in a vertical profile in the site Zajic in the Třeboň Basin. Levels of Mn, Zn, Ni, Cr and Pb decreased with increasing depth, the reverse state was found at cobalt. There was found a soft correlation between cobalt concentrations in peats and in surface waters sampled singly from the controlled sites.

A 4

DETERMINATION OF ALUMINIUM IN BEVERAGES BY AAS

T.Černohorský

University of Chemical Technology, Department of Environment Protection, Pardubice

At present the toxicologic importance of aluminium is shown serious, it can be seen marked especially in the case of the infusion solution and beverages. For these reasons the methodology of determination of low concentrations of Al by the method WETA AAS was worked out and the method of flame AAS was applied to determination of higher concentrations.

The method of WETA AAS takes advantage of tungsten electrothermal atomizer. The computer controlled atomization apparatus WETA 88 was used in our case in connection with spectrophotometer AAS 3 (Carl Zeiss Jena). The convenient temperature program was developed and in the same time the matrix influences were studied. It was demonstrated, that the mechanism of atomization in the tungsten atomizer is different from the mechanism in the graphite furnace. In the case of flavoured soda waters the content of the organic matrix was too high. So that the UV-photolytics mineralization had to be applied. This procedure proved to be very advantageous for this type of sample and reduced meaningfully the risk of contaminations.

For the determination of high contents it was suggested, that the direct injections of 5x diluted flavours soda water to the flame is possible, without the occurrence of interferences produced by matrix influences.

The measured results suggested the inconvenience of aluminium barrels for the storage of beverages. Concentrations in beers reached the values up to 10x higher than the standard, which is 0.2 mg/l. In the case of flavoured soda waters the measured concentrations were catastrophic, they exceeded the standard more than 500x. In the case of flavoured soda waters the kinetics of extraction from the aluminia barrels was studied.

QUALITY CONTROL WITH CRM´S FOR TRACE ELEMENT DETERMINATION IN CANDIDATE REFERENCE MATERIALS

Eva Čurdová, *Carola Mohl, *Peter Ostapczuk
National Institute for Public Health, Šrobárova 48,
100 42 Prague, ČSFR
*Institute of Applied Physical Chemistry, Research Center
(KFA) Juelich, P.O.Box 1913, D 5170, Germany

Determination of some trace elements in environmental samples for pollution control in east european countries is one of our major tasks. Bad financial situation makes it nearly impossible to use the available standard reference materials from BCR, NIES or NIST for routine quality control. In CSFR similar to other countries the necessity for the use of internal reference materials was soon recognized. Therefore some reference materials such as bovine liver, bovine kidney, bovine muscle, lyophilized bovine whole blood, rice flour, wheat flour and different soil samples were prepared by the Nuclear Research Institute (Prague), University of Agriculture (Prague) and Czechoslovak Institute of Metrology (Bratislava) |1|. These materials have been or will be certified soon. In our study these materials are brought into solution by pressurized decomposition with nitric acid in PTFE bombs at 180 °C and in quartz vessels at 290 °C. The analytical procedure for certification of the above listed reference material was checked by use of the following certified reference materials: SRM 1577a Bovine Liver (NIST), SRM 1568 Rice Flour (NIST), CRM 186 Pig Kidney (BCR), CRM 184 Bovine Muscle (BCR), Soil 5 (IAEA) and Soil 7 (IAEA).
Cu, Cr, Pb and Cd were determined by ETAAS in solution from PTFE bomb decomposition. Zinc was determined by ICPAES and by voltammetry. Since sample decomposition in PTFE bombs at 180 °C is not complete voltammetric determination can be done only for element concentrations higher than 100 /ug/kg. Therefore only in soil samples the voltammetric determination of Zn, Cd, Pb, Ni and Co was possible.
After pressurized decomposition in quartz vessels at 290 °C copper, cadmium, lead, zinc, nickel and cobalt can be determined without problems by voltammetry in all investigated samples.

Results of measurements in candidate reference materials will be presented.

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A 6

DETERMINATION OF THALLIUM IN SOLID EMISSION AND IMISSION SAMPLES USING AAS-ETA

M. Fara, Power Research Institute, Prague
M. Koželuh, L. Čermáková, Charles University, Prague

Among elements determined in solid emission and imission samples, thallium is classified in the group of the most toxic metals together with beryllium, cadmium and mercury.

The samples, analyzed as to the content of heavy metals, were digested and fumed off with the nitric, hydrofluoric and perchloric acids in consecutive steps and the resulting total solids were dissolved in the diluted nitric acid. The highest temperature applied did not exceed 200 °C to protect the light volatile elements (e.g. As, Cd, Pb) against the losses.

The imission samples were trapped on the membrane filters *Synpor* or *Nuclepore*. VARIAN 30P atomic absorption spectrometer together with GTA-96 graphite furnace was used.

Interference of nitric acid, increasing the atomization signal of Tl for almost 30% in 0.4 M HNO_3 medium (compared with the signal obtained in 0.1 M HNO_3), was overcome by using graphite platform. The graphite platform enabled the determination of 10^0-10^1 ppb of thallium in the presence of 10^2-10^4 ppb of Al, Ca, Cu, Fe, K, Mg, Pb, Si and Zn.

The following optimum temperatures and characteristics were found with the platform and 20 µl sample injection:

ashing temperature	500 °C
atomization temperature	2000 °C
detection limit	0.7 ppb
characteristic concentration	1.7 ppb/1% abs
characteristic mass	16 pg/1% abs
linearity of the calibration graph upward	800 pg.

In the reference material NBS 1633a *Coal Fly Ash* with the value of 5.7 ppb of thallium (certified by mass spectroscopy method), the content of 6.5 ppb of thallium was found.

The method developed was also applied to the determination of thallium in waste water, ash dump infiltrations and in ashes and their leaches.

A 7

DETERMINATION OF VANADIUM IN PETROLEUM PRODUCTS BY ETA-AAS AND ICP-OES

M.Fišera, Z.Hladký and J.Rišová

Faculty of Chemical Technology STU, Department of Analytical Chemistry, Radlinského 9, 812 37 Bratislava, Czechoslovakia

In toxicological, environmental and occupational health studies the measurement of trace elements is very important. Although it is known that vanadium is an essential trace element, possesing specific physiological functions, interest in this element is mainly on account of its toxic effects.

The discovery of high concentrations of vanadium in the fly ash from the combustion of petroleum products and coal has futher increased interest in the toxicity of vanadium compounds. Vanadium is important in petrochemical industry for its toxicity at high levels such as environmental pollutant and on the other side as an element adversely affecting catalyst activity and selectivity during cracking operations.

The use of ETA-AAS to determine vanadium in petroleum products suffers from the following disadvantages:
Formation of vanadium carbide during the ashing and atomisation steps with a resulting decrese in sensitivity and the problem associated with the calibration by the organic and inorganic vanadium compounds.

Possibilities of modification of ETA-AAS for direct analysis and after mineralisation step some petroleum products are presented. The results obtained by ETA-AAS were compared with results obtained by the application of ICP-OES method on dissolved samples in organic solution.

A 8

PURE BORON - USE OF AAS FOR THE DETERMINATION OF SILICON

V.Hamplová,Z.Málková,J.Novák
Institute of Physics Czechoslovak Academy of Science
Prague

Determination of small amounts of silicon in boron by direct AAS method with flame atomization in concentrations of 1 - 15 μg/ml in hydrochloric acid (concentration 0,25M) even at the 1000-fold weight excess of boron (concentration 1 mg/ml of boron) is described. Samples (0,1g) were decomposed in a silver crucible by melting with 1 g NaOH under an addition of $NaClO_3$ and the melt was dissolved in hydrochloric acid.

In contrast to some papers published hitherto, we have not observed under given conditions any effect of boron on the determination of silicon by the AAS method.

Dependences of the silicon signal on the boron content (up to conc. 0,1M solution of boron), on acidity of the solution (up to 0,5M hydrochloric acid), and on the content of NaCl were measured. Atomic absorption spectrometer VARIAN Spektr AA.30 with deuterium background correction was used. The silicon concentrations were evaluated from integrated absorbances on a 251,6 nm line.

The applicability of this method was verified on samples of technical-grade and pure boron (content of Si 0,05% - 2% w/w). The obtained results are identical with those achieved by a spectrophotometrical determination of silicon as a blue silicomolybdate complex.

ATOMIC SPECTROSCOPY DETECTORS FOR CHROMATOGRAPHY

Gy. Heltai

University of Agricultural Sciences, Department of
Chemistry, H-2103 Gödöllő, Hungary

The use of atomic spectroscopy detectors for chromatographic element specific detection has rapidly expanded over recent years. Combining the separating power of chromatography with high sensitivity and element selectivity of spectroscopy makes possible to exploit their complementary adventages. The present paper gives a survey of coupling possibilities of chromatography (GC, LC, SFC) with various forms of atomic spectroscopy (DCP-, ICP-, MIP-AES and AAS). Particular attention is devoted to microwave induced plasma atomic emission detection due to its excellent compatibility with many kinds of chromatography. The MIPs can be sustained with relatively low noble gas flows (0.05-2 l/min Ar, He or Ne) and at a moderate power (30-200 W). They are excellent emission sources for atomic emission detection because highly energetic species, particularly in the helium MIP promote the excitation of elements with high excitation energies (F, Cl, Br, I, O, S, N, P, C) which are hardly accesible with other sources. The new MIP-torches recently developed allow the realization of new MIP-configurations (toroidal, or suspended cylindrical discharges) which are very effective for sample introduction.

A 10

DETERMINATION OF GERMANIUM IN POLYESTER MATRIX BY INDUCTIVELY COUPLED PLASMA ATOMIC EMISSION SPECTROMETRY

Hezina F., Filipu P.*

Institute of Landscape Ecology, Czechoslovak Academy of Sciences,
České Budějovice

*Silon a.s., Research department, Planá nad Lužnicí

Determination of germanium is very interesting in polymer industry. Germanium is widely used as a polycondenzation catalyst. The resulted polyestars fibers have a better white colour then with antimony catalyst.

The methods for optimal decomposition procedure were dry ashing in the furnace and wet ashing by a mixture of mineral acids. The influence of various acid concentration on intensity of emission was studied. Dilute hydrochloric acid is promissing medium for highly sensitive detection in ICP AES, as the emission intensity for germanium significantly increases. Such an effect was not observed with nitric and sulfuric acid. The enhancement of sensitivity is attributable to the improvement in the efficiency of introduction of the analyte into the plasma caused by formation of volatile chlorides of germanium compounds. Spectral interference were studied by scanning of the analytical lines. No spectral interferences has been found. The accuracy of the measurement was expressed as a function of the relative standard deviation on the concentration of the analyte. The precision of the measurement was verified by independent spectrophotometric method and standard additions method.

The determination was performed on ICP AES spectrometer PU 9450, Leeman Laboratory - Philips with grid type nebulizer and echelle monochromator. The limit of detection for measurement and determination limits were 0.08 mg/l and 0.15 mg/l respectively.
The method is suitable to the determination of Ge in polyester matrix.

PARTICULAR PROBLEMS ENCOUNTERED IN TRACE ELEMENT ANALYSIS OF ENVIRONMENTAL SAMPLES BY ELECTROTHERMAL ATOMIC ABSORPTION SPECTROMETRY (ET-AAS).

Michel Hoenig

Institut de Recherches Chimiques du Ministère de l'Agriculture
Leuvensesteenweg 17, B-3080 Tervuren, Belgique
Tel. 322/767.53.01, Fax 322/767.72.88

At the present time the analyst is confronted with an increasing demand for greater sensitivity, reliability and speed to analyse complex samples. Modern technology has provided new concepts, procedures and instruments to deal with this growing demand.

This work describes several approaches we used to attain a real routine trace analysis of environmental samples using electrothermal atomic absorption spectrometry (ET-AAS). We present a discussion concerning ET-AAS analysis of sediments, suspended matter samples, plant and animal tissues, seawater, blood and urine : all these matrices necessitate different analytical approaches. The advantage and role of chemical modifiers are discussed for several typical examples. These classical approaches, using chemical modifiers in order to simplify the matrix prior to the analyte atomization, are compared with recently proposed "fast programmes", which consist of drying and atomization steps only and where the ashing step and the use of modifiers are avoided.

Also discussed are problems related to the sample preparation steps prior to the determinations. Interest is growing in the determination of elements in solid samples rather than in solution, thereby avoiding contaminations and losses of the analyte during these preparation steps. To avoid time-consuming mineralization procedures and the resulting above-mentioned problems, we have developed a robotized slurry sampling ET-AAS system. This fully automated procedure is actually employed for government programmes related to the pollution of marine sediments and suspended matter samples, which require the routine determination of eight trace elements (Cd, Co, Cr, Cu, Mn, Ni, Pb, Zn) and two main matrix elements (Si, Al).

A 12

ICP-MS INSTRUMENTATION AND APPLICATIONS IN ELEMENTAL TRACE ANALYSIS AND ISOTOPE RATIO MEASUREMENTS

R. C. Hutton(1), Amanda Kingston(1), P. A. Freedman(2), A. J. Walder(2) and I. Platzner(3)

(1) VG Elemental, Fisons Instruments, Ion Path, Road Three, Winsford, Cheshire, CW7 3BX, UK
(2) VG Isotech, Fisons Instruments, Aston Way, Middlewich, Cheshire, CW10 0HT, UK
(3) NRCN, P O Box 9001, Beer-Sheva, Israel. Visiting scientist at VG Elemental, Winsford, Cheshire, UK

Inductively coupled plasma mass spectrometry (ICP-MS) has become a well established method for multi-element trace analysis. It originated in the early 80's by interfacing an ICP argon ion source and a quadrupole mass spectrometer with an ion extraction system. The technique yields relatively simple mass spectra, features detection limits in the ppt region and has a capability of isotope ratio analysis. Isotopic overlaps, double charged oxide and other polyatomic ions at amu <80 may interfere with simple data interpretation.

A further development in ICP-MS is the coupling of the ICP ion source to a double focusing magnetic sector mass analyser [1]. The advantage of a high resolution ICP-MS over the quadrupole are the following:

(1) Lower background and higher ion transmission; thus improved detection limits.
(2) Mass resolution of up to 10.000, thus the capability of resolving ions under investigation from interferences.
(3) Flat top peak shapes compared to the round top quadrupole peak shapes, thus improving the measured isotope ratio precisions.

The high resolution ICP-MS, the VG PlasmaTrace has extensive applications in many areas of analytical chemistry. In this presentation the following examples will be discussed. Determination of the elements as Mg, Al, S, Ca, Cr and Fe in high purity organic solvents. Determination of trace elements in acids in the semiconductor industry. Environmental applications, as determination of elements in ground water, snow and waters from various sources. Analysis of trace elements in solids with laser ablation. Determination and detection limits of rare earth elements [2].

A double focusing ICP-MS, equipped with seven Faraday detectors has recently been used for isotope ratio measurements [3]. NIST (Washington, USA) Isotopic Standard Reference Materials of uranium, lead and strontium have been analysed. Relative standard deviations (RSD) of 150ppm (1σ) for the ^{235}U/^{238}U ratio have been observed. Six samples of the SRM Pb-981 and Pb-982 yield RSD values in the range 220ppm for ^{208}Pb/^{206}Pb and ^{207}Pb/^{206}Pb to 540ppm for ^{204}Pb/^{206}Pb, compared to the NIST values of 180-490ppm, obtained with triple filament thermal ionization mass spectrometry. The measured ratios demonstrate a constant bias factor per amu of 0.8%, which originates from preferential transport of the heavier isotopes into the mass analyzer. This means a standard of known isotopic composition must be analyzed prior to the sample analysis to determine the magnitude of the bias. In the measurements of the ^{87}Sr/^{86}Sr ratio, where the internal normalization method for bias correction is applicable, high accuracy data with 80ppm RSD (10 samples) are obtained. Further work on isotope ratio measurements with the double focusing isotope ratio mass spectrometer is now in progress and will be presented.

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DETERMINATION OF INORGANIC POLLUTANTS IN DRAINAGE AREAS OF THE BĚLÁ AND SEMÍČ STREAMS

V. Kanický, J. Budiš and M. Soldán
Faculty of Education of the Masaryk University in Brno, Department of Chemistry, Poříčí 7, 603 00 Brno, ČSFR
D. Kolčava, J. Toman
LABTECH, Ltd., Polní 23/25, 639 00 Brno, ČSFR

Quantity and quality of drinking water for the south-moravian metropolis Brno depends on water resources of the Czech-Moravian Highlands and the Drahanska Highlands. Demands for supplying with water are still increasing and discrepancies between the need and the capacity of water resources are escalating.

Unfavourable condition is caused by permanent deterioration of water quality as a result of contamination by human activities. This harmful situation can be improved, among others, on the basis of complex monitoring of inorganic and organic pollutants in surface water, followed by detecting the sources of this contamination.

A project for the monitoring of pollutants and the locating of their sources has been created at the Faculty of Education of the Masaryk University in Brno. The first stage of this work consists in the analytical data acquisition but the final stage should include some recommendations for remedies.

We have started with the determination of trace metals in the river water of the Bělá and the Semíč streams, the tributories of the Svitava river. They are situated in the eastern part of the river basin of the Svitava middle stream. The investigated region covers the area of 120 sq. km and comprises an agricultural land, an industrial agglomeration with considerable concentration of inhabitants (town Boskovice) and an afforested landscape. Presented results show considerable differencies between these areas and probably indicate the sources of contamination.

The samples were analysed in the laboratory of LABTECH, Ltd. in Brno, formerly UNIGEO. Metals were determined using FAAS, ETAAS, CV-AAS, HG-AAS and OES-ICP (Varian 875, Philips PV 8490/8210).

A 14

ANALYSIS OF HIGH-TEMPERATURE SUPERCONDUCTING FILMS BY XRFA AND ICP AES

V.Kliment

Institute of Physics,Dúbravská cesta 9,84228Bratislava

The properties of high-temperature superconductors depend on chemical composition and also on concentration of impurities in these materials.Therefore,a precise analytical method is need for finding the best condition of their preparation and testify composition of the sample.This requirement is more urgent in the preparation of high-temperature superconducting films.The mass of these films deposited on suitable pad is small and often is smaller than 100 μg.We have used ICP AES and XRF analysis for analysis of $YBa_2Cu_3O_{7-x}$ superconducting films.

An atomic emission ICP spectrometer JY 70 VHR was used for determination of Y,Ba and Cu in the sample solutions.The samples for atomic emission determination were dissolved in diluted HCl. The emision lines 324754 pm,371010 pm and 233527 pm were used for determination of Cu,Y and Ba,respectively.Manganese was used as an internal standard (λ =257610 pm) to improve the precision of analysis.

The ^{241}Am source was used for excitation in case nondestructive determination by XRF analysis.The characteristic X-ray of elements was detected by Si(Li) detector and X-ray spectra were registrated by a 1024-channel analyzer.The AXIL computer program was used for evaluation of X-ray spectra.

The comparison of the results of both methods testifies to an acceptable agreement between ICP AES and XRF analysis.

A 15

DEPTH-PROFILING WITH GLOW-DISCHARGE OPTICAL SPECTROMETRY

V.Kliment

Institute of Physics,Dúbravská cesta 9,84228Bratislava

Glow-discharge optical emission spectrometry may be used for depth-profile analysis of thin-film samples.The thin sample in contact with cathode is continuously sputtered by positive accelerated argon ions.The atoms of the sample are ejected and accelerated towards the anode.They meet the electrons and collisions between them result in emision of light.This light,with the different wavelengths for each element in the excited sample,is then analysed by spectrometer.

We have constructed simple glow-discharge lamp and in connection with Jobin-Yvon 70 VHR spectrometer we searched for the optimal experimental conditions in depth-profiling of different element films on the metallic pads.The dependences of the intensities of emitted light on the energy of accelerated argon ions, current of argon ions and pressure in the discharge lamp were studied to obtain maximum sensitivity and the best depth resolution.

DETERMINATION OF TRACE LEVELS OF SOME TOXIC METALS IN BIO - CERAMIC MATERIALS BY ETA - AAS

Kolihová D.,Vyskočilová O.,Doležal J., Švorčíková J.

Department of Analytical Chemistry and Central Laboratories
Institute of Chemical Technology
Technická 5, 166 28 Prague 6, Czechoslovakia

The bio - ceramic materials used as substitution of bones in human medicine has been tested with respect to the content of two toxic elements - lead and barium. Atomization from both a graphite furnace and a tungsten tube atomizer has been compared. Interferences from two main matrix components (calcium and phosphate) have been studied. Different chemical modifiers have been evaluated.

The Varian SPECTRAA-300Z instrument with GTA-96 graphite tube atomizer and Zeeman effect background correction, pyro-coated graphite tubes and peak area measurement were used. All measurements were compared with those carried out by means of tungsten tube atomizer WETA-90 and Varian AA-775 with deuterium background correction.

The optimum working conditions, detection limits, as well as accuracy and precision are discussed.

A 17

DETERMINATION OF ARSENIC IN WATER USING CONTINUOUS HYDRIDE GENERATION AND EXCITATION IN THE PLASMA SOURCE BY MARINKOVIĆ

L. Koller
Department of Chemistry, Technical University, Košice

Arsenic is a toxic element widely distributed in the environment. The limit of concentration in drinkong water is stated on the value of 0.05 mg.l^{-1}. Systematic control of arsenic concentration in drinking water requires application of a simple and efficient analytical method with the detection limit value less than 1 ng.ml^{-1}.

A continuous hydride generation system is set of a two-channel peristaltic pump, reaction tube, stripping coil and a conventional spray chambre as the phase separator. The released covalent hydride is transported by the argon carrier gas into the plasma source by Marinković. The emission signal is detected using sequential spectrometer. The argon flow rate, the sample acidity and uptake, and the plasma position were optimized from the aspect of maximum value of signal to background ratio. Simultaneous pneumatic nebulization of distilled water causes the decrease in background intensity. This phenomenon is more expressive in the case of the nebulization of the solution containing easily ionized elements. Optimum concentration of the nebulized solution is 0.2 mol.l^{-1} $NaNO_3$.

Utilizing optimum experimental conditions a simple method for arsenic determination have been developed with detection limit (3s) of 0.5 ng.ml^{-1} and relative standard deviation (at 50 ng.ml^{-1}) of 1.7 %.

A 18

SOME SPECIFIC PROBLEMS IN ENVIRONMENTAL ANALYSES

Ľ.Korpeľ and J.Vozár

Geological and ecological laboratories (GEL), Spišská Nová Ves, ČSFR

Environmental analyses are a broad term. In GEL laboratories are completely worked up samples of soils, waters, stream sediments and biological materials. It includes sampling, homogenization, analyses and interpretation of results.

Analyses of such types of samples have some specifics as :

1. An analyte at levels from 0,1 to 10 ppm in sample
2. Required a very low limit of detection
3. During analyses must be used hight purity chemicals
4. The most sensitive methods must be used
5. Laboratories and laboratory equipments must be especially clean to avoid contamination

Methods utilizated in GEL :

Sample decomposition - wet digestion using acids or their mixures (HCl, HNO_3, H_2SO_4, $HClO_4$, HF). It depends on type of determination and materials.

Instrumental technique - we use a broad spectrum of analytical methods as :

AES-ICP	Atomic emission spectroscopy with inductively coupled argon plasma
AAS-ETA	Electrothermal atomic absorption spectroscopy
AAS-HG	Atomic absorption spectroscopy with hydride generation
AAS-ACT	Atomic absorption spectroscopy with preconcentration tube ACT 80 (fy VARIAN)
FAAS	Flame atomic absorption spectroscopy
RFA	X-ray fluorescence analysis

We have reached good limit of detection (DL) for all elements which are required in ecological projects. The comparison of DL achieved in GEL and required DL by WEGS (Western European Geological Surveys) in environmental analyses for some elements is in the next table :

Element	Method	Detection limit(ppm)(1)	(2)
As	AAS-HG	0,1	1
Bi	AAS-HG	0,1	0,1
Cd	AAS-ETA	0,005	0,1
Co	AAS-ETA	0,04	1
Cr	AAS-ETA	0,015	35
Pb	AAS-ACT	2,5	7
Sb	AAS-HG	0,1	0,1
Se	AAS-HG	0,1	0,1
Te	AAS-HG	0,1	0,1
Tl	AAS-ETA	0,1	0,8

1-achieved in GEL 2-required for projects of WEGS

The values of DL are in solid samples.

Accuracy of methods used in GEL was verified by analyses of NIST standard reference materials.

A 19

DETERMINATION OF Cd, Pb AND Mn BY WETA 88 AND INFLUENCE OF CHEMICAL MODIFIERS

Krakovská Erika, Department of Chemistry, Faculty of Metallurgy,
Technical University Košice.
Puliš Pavel,Air Force School Košice.

With atomization from tungsten surface advantageous values of characteristic mass can be achieved for many elements, not only for elements forming hard-decomposing carbides or oxides.

While determining elements as Cd and Pb it is necessary to use such chemical modifiers, which act as thermal stabilizers during thermal pretreatment of the sample. Considering the fact, that acting of the same chemical modifiers in the tungsten atomizer needn´t be the same as in graphite furnace, acting of more materials which are suitable for this purpose was studied.

While determining Cd, influence of $NH_4H_2PO_4$, H_3PO_4, $La/NO_3/_2$, $Pd/NO_3/_2$, of the mixture $La/NO_3/_3$, and $Mg/NO_3/_2$ was studied, while determining Pb influence of $NH_4H_2PO_4$, $Pd/NO_3/_2$,$Mg/NO_3/_2$and $La/NO_3/_3$ on the value of the temperature of the thermal pretreatment of the sample, as well as on the height of the absorption signal, was studied. While determining of Mn, influence of $Mg/NO_3/_2$ $Pd/NO_3/_2$ and the mixture $Mg/NO_3/_2$ and $Ca/NO_3/_2$ on the value of the absorption signal was studied. In separate modifiers their optimum concentration was determining and their buffering effect in certain types of chemical interferents was studied.

It was stated, that the values of thermal pretreatment temperattures of the sample while using the same modifiers in tungsten furnace, are achieving lower values, than in graphite furnace.

A 20

DESORPTION OF ZINC FROM SOILS BY SELECTED ORGANIC COMPOUNDS

S. Krištoufková, J. Jehlička, J. Kozák
University of Agriculture, Prague

The concentrations of zinc extracted from seven soil samples by organic compounds of different concentrations were determined. The extracted amounts of zinc were compared with those gained by using standard extraction procedure i. e. 2 M HNO_3.

Extractions were done by urea (0.02, 0.01, 0.005 M), EDTA (0.02, 0.01, 0.005 M) and L-serin (0.01, 0.005, 0.0025 M). The soil samples were taken from the following soils:

Calcaric Phaeozem	Hc	(cPH)	locality Macov
Calcic Chernozem	Ck	(cCH)	locality Čáp
Eutric Cambisol	Be	(eCA)	locality Krompachy
Albic Luvisol	La	(aLU)	locality Prašice
Orthic Luvisol	Lo	(oLU)	locality Čechy
Calcic Chernozem	Ck	(cCH)	locality Báhoň
Calcaric Phaeozem	Hc	(cPH)	locality Macov uncontaminated

Desorption was done in three steps. First desorption was performed by destilated water only. The second and the third desorptions were done using organic compound of the same concentration. Three grams of soil were shaken with the extractant solution on the reciprocal shaker for 18 hours. After centrifugation and decantation of supernatant another portion of supernatant was added and the described procedure was repeated. Water and urea extracts were stabilized by adding HNO_3.

The concentrations of zinc in all supernatants were determined by the means of atomic absorption.

Water, urea and L-serin at the range of concentrations used in this study didn't desorb detectable amounts of zinc. EDTA desorbed much higher amounts of zinc; repeated desorptions were less efficient than the first one. Only with some soil samples the positive relationship between concentration of extractant and the concentration of desorbed zinc were found.

In all cases 2 M HNO_3 caused many times higher rate of zinc desorption in comparison with EDTA.

A 21

HEAVY METALS STRATIGRAFY IN VERTICAL PROFILE OF FISHPOND VAJGAR SEDIMENT

E.Kroupa, J.Bastl
Jihočeská Universita, Zemědělská fakulta, katedra chemie,
České Budějovice

This paper presents the results of analysis of heavy metals in a vertical profile of sediment in the fishpond Vajgar in the town Jindřichův Hradec,SE Bohemia.

The following metals Cd,Co,Cu,Cr,Fe,Mn,Ni,Pb and Zn were estimated in 2.40 m deep sediment profile subsampled into 42 layers.Both total concentration and fractionation of a metal were determined in the particular layers.

Total concentrations of heavy metals in sediment were determinated by atomic absorption spectroscopy using an air-acetylen flame with Spectra 10 Varian apparatus.Lead and cadmium were determined with AAS-3 analyzer using a tube furnace atomic absorption spectroscopy.

Heavy metals were fractionated by the method described by TESSIER (1979).Five fractions of heavy metals were determined by atomic absorption spectroscopy after gradual agitation of the sediment with different extractants.

Heavy metals in vertical profile showed large range of concentrations.Following range of concentrations (mg.kg^{-1}) in the core of sediment were found: Mn 303-1240; Fe 15 800 - 42 000 ;
Zn 122 -381; Pb 22.2-87.3; Ni 11.7-40.2;Co 13.9-30.1; Cu 11.0-85.33;Cr 13.3-40.3; Cd 0.00-2.16.

Concentrations of heavy metals were generaly the lowest in the deepest layers of the profile (between 200-240 cm of the depht).

The ratios of metals in fractions were following:the most of the metal were found in the fifth fraction-namely in deeper layers.Copper was bound extensively to organic matter(about 40%).

The large proportions of zinc,lead,iron,manganese and chromium were bound to manganese and iron oxides.30% of manganese in the top layer of the sediment were determined as exchangeable (i.e.first fraction).

FIRST EXPERIENCES AND THE PERFORMANCE SH-AAS 4000

Kubizňáková J., Láznička P.

Ústav krajinné ekologie ČSAV, České Budějovice

The use of atomic spectrometry for monitoring of trace elements in environmental samples (air, water, soil, plant, animal tissues) are now well established and widely practised. After dramatic developments during more than 30 years in atomic spectroscopy the prominent amongst is directed for simultaneous *multi-element determination and also for direct analyses with* minimize sample preparation. All such suggests of the demands for monitoring of trace element in the environment need compress down by the financial cost.

One relative new techniques appears in U.S.A. (1), and it have achieved also our country. This techniques offers unattended multi-element determination and fully automatic operation. High performance Smith-Hieftje background correction has recommended to perform analyses to EPA standards.

In the present ,it will be described some characteristics, some preliminary results with and without SH-background correction and also first experiences with this for us the new instrument, which it's first in Czechoslovakia .

Reference:

S.B.Smith, G.M. Hieftje,: A new-Background-correction.Method for Atomic Absorption Spectrometry, Appl.Spectroscopy, 37 (5), 419-424 (1983)

Operational manual TJA for SH-4000, and CTF 188

Atomic Absorption Methods Manual

A 23

DETERMINATION OF Ta AND Nb AT LOW LEVELS IN GEOLOGICAL MATERIALS BY OES ICP

Kubová J., Polakovičová J., Streško V., Medveď J.

Geological Institute, Faculty of Natural Sciences,
Comenius University, Bratislava

Low contents of Ta and Nb cannot be determined by OES ICP in different geological materials using only one recommended standard procedure. For individual types of samples showing a great variability of their macrocomposition, following three fundamental problems have to be solved:

- To find a suitable decomposition of the sample in question and to ensure the stabilization of Ta and Nb in the obtained solution.
- To choose a suitable separation - preconcentration procedure (which can be omitted only in few cases) removing or essentially lowering the content of interferents (namely Fe) in the solution which has to be analyzed.
- To perform a comprehensive study of spectral interferences occuring at optimum conditions for the OES ICP determination of Ta and Nb (viewing height, plasma power, gas flow rates etc.) and to propose a suitable procedure for their correction.

In the present work a procedure for the determination of Ta and Nb in granites without any separation - preconcentration and in biotites where a separation - preconcentration step is necessary, is presented. A correction of spectral interferences on the selected Ta and Nb spectral lines is performed.

The proposed procedure was checked by the analysis of real samples using and other analytical method (INAA), as well as by analyzing attested reference materials.

A 24

SHORT STUDY ABOUT INFLUENCE OF MATRIX CONSTITUENTS IN ANALYSES OF ANIMAL TEETH

Láznička P., Hezina F., Kubizňák J.

Ústav krajinné ekologie ČSAV, České Budějovice

Teeth could be an interesting marker for trace elements, because we can find a lot of old ones as hunting trophies. At first we need to know the contents and influences of particular elements. Problems in analyses is based especially in high contents of calcium phosphate. Serious problems are high salinity and matrix interferences, what's limited advantages of ICP OES For the use of analyses we are compared some ways of preparing samples and their analyses. The first is separation on the strong cation-exchange resin Bio Rad AG-MP-50, preconcentration on rotary evaporator and determination using ICP OES . The second is direct measuring of diluted samples using flame AAS with D_2arc background correction and method of standard additions. The third is using solvent extraction of Ca by 8-Hydroxychinoline and measuring on PU 7450 ICP OES. We have also possibility to compare these results with those by methods GF ETA AAS with Smith-Hieftje background correction. Using cation-exchange resin has advantage in removing P and decreasing content of Ca. This is usefull for measuring ICP OES, but preconcentration brings inaccuracies with used acid, cation-exchange resin and during evaporation.

The determination of the low concentrations of aluminium in steel on optical emission and XRF spectrometers

Ing. Ivana Loskotová,
Ing. Václav Helán, Třinecké železárny, a.s. chemické zkušebny

Ing. Dagmar Fáblová,
Hana Pixová ZVÚ Hradec Králové

After the start of the continuous casting in Třinec Iron and Steelworks, there was used also the free aluminium technology. The highest acceptable level of whole Al was changed (reduced) on 0.003 % Al in steel C72K9 (cs standard ČSN 12).

The determination of aluminium in steel is performed on the optical emission spectrometers fy ARL, but so far the higher concentration of aluminium were analysed. There was the a problem with the repeatability of the single determination of aluminium below 0,005 %.

At first we controled the short - term and the long - term stability of spectrometer on ČKD 101H standard of low - alloy steel with concentration of aluminium 0,04 %. We found out, that the stability of spectrometer is correct. The highest differences between single determinations were obtained after recalibration of spectrometer and the repeated measuring of low setting up standard was not reproducible. The relative standard deviation of pure iron sample with 0,004 % Al was 47 % and finally we derived from this, that the sample surface of the soft material is contaminated from the grinding paper by Al2O3.

We tested four methodes of the sample preparation for different steel qualities on the disk grinder fy HERZOG and there were : the grinding on the emery (grinding) paper (grain size 60) with and/or without alcohol rinsing of the sample surface and the grinding on the carborundum paper (grain size 60) also with and/or without alcohol rinsing of the sample surface. After that the samples were measured on OES ARL 177 RETB and ARL XRF 8680.

On optical emission spectrometer the best results were obtained by using of the sample preparation on carborundum grinding paper and the highest differences between the using carborundum or emery paper were obtained in cases of pure iron (low setting up standard) and some qualities of low-alloy steels. The important differences of the determination repeatebility were not discovered in cases of the middle-alloy steel and of the high-alloy steel. The influence of the alcohol rinsing was not perceptible.

On XRF spectrometer we obtained the best results also by using of carborundum paper and the influence of the alcohol rinsing was higher than on optical emission spectrometer.

QUARTZ TUBE ATOMIZERS FOR HYDRIDE GENERATION AAS: INTERFERENCES IN THE SELENIUM HYDRIDE ATOMIZATION

T.Matoušek and J.Dědina

Institute of Nuclear Biology and Radiochemistry, Czechoslovak Academy of Sciences, Vídeňská 1083, 142 20 Praha 4.

The origin of interferences of arsine, stibine, stannane and methane in the selenium hydride atomization in quartz tube atomizers was studied. Two- or four-channel continuous flow hydride generation system was used to eliminate liquid phase interferences. Two quartz tube atomizers were employed: (i) a "hybrid" atomizer having features of a flame-in-tube atomizer as well as of an externally heated quartz tube atomizer and (ii) an atomizer with two inlet arms designed to separate spatially the atomization of the analyte and the interferent. The influence to the extent of interferences of the purge hydrogen flow rate, the oxygen supply, the atomizer temperature and the distance of the oxygen delivery capillary from the optical tube was investigated.

There was no principal difference neither in nature nor in extent between interferences observed in the "flame-in-tube atomizer" and in the "externally heated quartz tube atomizer" arrangement. Increasing the oxygen supply as well as the purge gas flow markedly decreased the interference magnitude. Memory interferences were effectively eliminated at temperatures above 600 °C. There was no evidence found for the radical population type of the atomization interference in the "flame-in-tube atomizer" version of the employed experimental set-up. Mechanisms of the observed interferences will be discussed.

A 27

THE DETERMINATION OF LEAD IN NEW CZECHOSLOVAK BIOLOGICAL REFERENCE MATERIALS OF ANIMAL ORIGIN

D. Miholová, J.Száková[a], J. M. Bellama[b], P. Mader, J. Cibulka
University of Agriculture, 165 21 Prague (Czechoslovakia)
[a]Agricultural Enterprise, 503 03 Smiřice (Czechoslovakia)
[b]Permanent address: Department of Chemistry, University of Maryland, College Park, MD 20742 (USA)

Interlaboratory comparisons of the determination of trace elements in biological materials have shown that many participating laboratories, despite acceptable precision, were not able to produce accurate results for such risk elements as lead. In 1991 we participated in the preparation and analysis of Bovine Kidney and Bovine Muscle, new Czechoslovak reference materials (RMs). Interlaboratory testing will be completed in 1992. RMs Bovine Kidney and Bovine Muscle were decomposed both by classical dry ashing and also in an Dry Mineralizer Apion (Tessek, Ltd.). Flameless AAS was used for the determination of Pb content in digests prepared from both tissues. In addition, the content of Pb in these materials was also measured by an independent electroanalytical method, DPASV. To assess the accuracy, we analyzed CRMs BCR-184 (Bovine Muscle) and BCR-186 (Pig Kidney), which have similar matrixes, simultaneously with the new Czechoslovak RMs.

We found that matrix effects on the determination of Pb by ETAAS are much more severe in analysis of **kidney tissue** than in liver tissue (see (1)). While the determination of Pb content in liver is possible with suitable dilution of samples from calibration obtained from the concentration curve, accurate values for Pb content in kidney can be obtained only from calibration by standard additions. Thus, utilization of the standard operation procedure (SOP) developed for determination of Pb in liver can lead to underestimation of Pb content in kidney. Since matrix effects on determination of Pb by ETAAS in **muscle tissue** are comparable with those in liver, a SOP developed for liver would also be applicable for the determination of lead in muscle. However, Pb content in muscle is lower than in liver, and at the dilution of the digest recommended for liver (15 mg of dry material per 1 mL of final solution), Pb concentrations found in diluted muscle digests are very often lower than the detection limit of the method (0,5 ng Pb.mL^{-1}. For these reasons, evaluation of low lead content in muscle tissues is possible only in less diluted digests and by the method of standard additions.

(1) Miholová, D., 1990. In: Využití atomové absorpční spektrometrie v potravinářské a zemědělské praxi. Pavelka J. (ed.), VUPP, Praha, p. 126

A 28

ANALYTICAL DIAGNOSTICS IN ICP - OES

Novotný I., Mermet J.M.*
Přírodovědecká fakulta Masarykovy university, Brno
*Université Claude Bernard Lyon, Villeurbanne

The optimal analytical conditions in the ICP - OES is complex of many variables depending on physical and chemical properties of both experimental system and analyte. However, these conditions are usually met only if the LTE is reached.

There are several methods to determine closeness to the LTE but analytically, one of the most usefull is the measurement of ionic and atomic lines ratio e.g. MgII 280.270/MgI 285.213.

Influence of several experimental variables (forwarded energy of 800 - 1600 W, frequency 27 and 40 MHz, amount of the introduced analyte varying from 0.4 - 1.5 ml/min, inner gas flow rate 0 - 1 l/ min, Meinhard, conespray and V - type nebulizers and especially influence of anions of easily ionized element) on MgII 280.270 / Mg I 285.213 as well as on lines with different spectrochemical properties (ZnII 206.19, BaII 233.53 and BaII 455.49 will be shown. These effects are profound under low energy conditions. Changes in the theoretical value of MgII 280.270 / MgI 285.213 as well as changes in optimal signal positions for different lines are discussed.

Conclusions for practical analytical work will be drawn.

A 29

USE OF MICROWAVE RADIATION FOR SURFACE WATERS ANALYSIS

Tomáš Paukert
Czech Geological Survey, Malostranské nám. 19, 118 21 Praha 1

The behavior of trace elements in various ecological systems is often an important part of geochemical studies. For some time the Czech Geological Survey has been monitoring precipitation and surface waters in selected regions. Not considering a good QA and QC in a laboratory, still many physical and chemical phenomena must be taken into account, e.g. proper sampling, sample storage, analytical determination, etc., while doing water analysis.

However, surface waters often contain microscopic particles of dust, as well as biological or organic materials. Immediate outdoor analysis is almost impossible and filtering may retain certain portions of an analyte. Some elements desire preconcentration such as ion-exchange, extraction or coprecipitation. To avoid contamination, some waters may be acidified and analyzed directly by an instrumental technique.

This experience inspired analyses of acidified samples of surface waters by FAAS or ETAAS after microwave digestion in a closed system. The results showed a remarkable increase of the elements of group III A and IV A of the periodic table of elements. Concentrations of group I A and II A did not change, except for Li. Although "heavy" metals are usually present in contents of $\mu g.l^{-1}$, they increased significantly with respect to the ETAAS measurement sensitivity. The increase in the concentration is most likely caused by a quick dissolution of particles deposited during a precipitation event. Moreover, using HCl as a reducing agent, the procedure suggested may convert environmently interesting Se^{VI}, (Te^{VI}) into Se^{IV}, (Te^{IV}) which can be determined by the HGAAS.

Thus mass balances needed for atmospheric bulk deposition will reflect better results.

A 30

DETERMINATION OF SILVER, GOLD AND PLATINUM METALS IN MULTICOMPONENT SWEEPS BY ICP SPECTROMETRY

S.Průcha
SAFINA s.p. Vestec, Jesenice u Prahy

This application combines OES-ICP method with fire assay technique. Precious metals collected in the lead button are successively dissolved in nitric acid and aqua regia. Resulting solutions are measured with the spectrometer PV 8065 Philips.

Sweeps are powdered industry wastes, where concentrations both precious and nonferrous metals are quite variable. So the thorough knowledge of spectrum and a careful selection of suitable sets of emission lines is necessary. There are described some matrix mutual interference effects and ways of their elimination. The accuracy of results is controlled by the gravimetric determination of the total of PM with kalomel.

The method is applicable even for the analysis of alloys, but in any case concentrations each measured element must be under 20 %.

The example of a procedure is given and results are compared with the chemical gravimetric analysis.

DETERMINATION OF BERYLLIUM IN ENVIRONMENT BY ETA-AAS AND ICP OES METHODS

J.Rišová, Z.Hladký and M.Fišera

Faculty of Chemical Technology STU, Department of Analytical Chemistry, Radlinského 9, 812 37 Bratislava, Czechoslovakia

An estimated some 1000 kg of beryllium is released annualy into ambient atmosphere of CSFR through the combustion of coal, mainly in form of its oxide. The other source of beryllium in environment are phosphorus-containing fertilisers. Studies of the possible relationship between exposure to soluble beryllium compounds and occurence of cancer (lung, skin or bone) in human and animals are reported. The pathogenicity of beryllium oxide depends on the firing temperature. Dusts produced at 1500 °C are much less toxic as dusts calcined below 500 °C.

Samples of beryllium containing materials (flying ash emissions, filters or fertilisers) were mineralised under pressure of 2 MPa and at 170 °C in container with mix of HF and HNO_3. After mineralisation and evaporation of SiF_4 and HF were samples diluted and analysed. For determination by ETA-AAS was exploited SP-9 atomic absorption spectrometer with totally pyrolytic cuvette at λ=234,9 nm, bandpass 0,5 nm and atomisation temperature 2600 °C.
Linear calibration graph was observed for 0,1-1,0 $ng.ml^{-1}$ range. For results evaluation was used standard addition method too.

An ICP-OES model ARL 3510 was used for determination by atomic emission spectrometry. Some obstacles of spectral interferences of many matrix elements were observed. The best beryllium emission line is lying at 313,107 nm.

Results obtained by ICP-OES and ETA-AAS for analysed samples of coal ash (approx. 1ppm) and fertilisers were in good agreement.

A 32

THE CONTENT OF Mn, Fe, Cu AND Zn IN THE FOODSTUFFS OF A PLANT ORIGIN IN SOUTH BOHEMIA

V. Rohlík, V. Kroupová, Z. Klein and J. Bastl

Department of Anatomy and Physiology, Agricultural Faculty, University České Budějovice, Czechoslovakia

As the content of trace elements in basic fodder crops also depends upon inconstant factors a continual analytical control is necessary to avoid an inadequate intake of them. During the years 1988-1990 in the region of South Bohemia with a low level of industrial pollution the contents of tested elements were below risk limits. On the other hand the amounts of Zn and Mn in the foodstuffs of a plant origin are relatively low and can not satisfy their requirement for cows with higher milk production. The necessary intake of these trace elements is possible to reach by a supplementation of convenient mineral mixture only.

Average values of trace elements content in the fodder:

Analysed material	mg/kg dry matter			
	Mn	Fe	Cu	Zn
hay	51,04	210,09	8,24	26,18
grain mixtures	34,43	189,99	5,93	26,56
clover	45,24	199,25	10,60	28,05
pasture	34,34	269,24	9,57	40,42
grass	38,23	204,14	6,26	21,24
flax grain	25,44	373,86	14,43	50,78
haylage	59,26	480,50	8,31	28,48
maize silage	20,38	243,29	4,11	19,18
straw	25,48	273,35	5,58	20,05
cabbage	27,30	302,40	3,71	23,45

A 33

THE DITHIZONE - POLYURETHANE FOAM SYSTEM USING AS A PRECONCENTRATION STEP FOR THE DETERMINATION OF Pb BY FAAS IN SOILS AND SURFACE WATER.

Rychlovský P., Bílý J. and Denková P.

Department of Analytical Chemistry, Charles University,
Albertov 2030, CS - 128 43 Prague 2, Czechoslovakia

Direct FAAS determination is possible for only a restricted number of trace elements in water and acidic extracts. Preconcentration prior to quantification of the element is needed in most cases. Various methods are used to preconcetrate trace metals. Recently complexation with organic reagents supported or immobilized on various supports becomes increasingly popular, on account of high selectivity, simplicity and effectiveness.

The determination of Pb by FAAS after the preconcentration on the column filled with polyurethane foam was developed. The method was based on the sorption of lead ions on diphenylthiokarbazone immobilized polyurethane foam and their elution by the mineral acid. The optimum conditions for sorption and desorption (the sorbent capacity, the dependence of the sorption efficiency on the pH values, the optimum sorption and elution flow rate, etc.) were discussed. The influence of interferring ions, like a copper, mercury, phosphates, was treated. The utility of the method was verified on the acidic soil extracts and surface water samples.

A 34

SAMPLES, SIGNALS AND NOISE IN INDUCTIVELY COUPLED PLASMA SPECTROMETRY

B L Sharp

Department of Chemistry, Loughborough University of
Technology, Loughborough, Leicestershire LE11 3TU, UK.

The presence of noise in any measurement system both determines the smallest signal that may be measured and limits the precision of measurement of any particular signal. Limited precision is a particular problem in ICP spectrometry because the noise is proportional to the signal magnitude. Moreover, the nature of the proportional noise is such that it cannot be reduced to any arbitrary level by extending the measurement period. Limited precision has restricted the application of ICP spectrometry for the determination of major elements and in the case of ICP-MS, has prevented it from competing more effectively with techniques such as thermal ionisation mass spectrometry for the determination of isotope ratios.

This paper discusses the origins of the noise encountered in ICP spectrometry and the manner in which the interaction between the sample and the instrumental system influences the noise observed in the analytical data. Two approaches to noise reduction will be considered, system improvement and signal processing.

A 35

PROBLEMS OF THE SOIL EXTRACTION

V.Spěváčková, K.Kratzer, M.Čejchanová
Technical University of Prague
Department of the Nuclear Chemistry

The problem of the behaviour of some heavy metals in forest soils during leaching procedure was studied. Method of atomic absorption spectrometry was used for the determination of the content of heavy metals in soils, radiotracers method was used for the study of the sorption and desorption processes.

DETERMINATION OF ELEMENTS FOR CERTIFICATION OF REFERENCE SOLUTIONS

Streško V., Medveď J., Kubová J., Polakovičová J.

Geological Institute, Faculty of Natural Sciences,
Comenius University, Bratislava

Metrological claims concerning the work of recent analytical laboratories using in a large extent different, mainly optical and electrochemical procedures require certified reference solutions with attested contents of elements.

The Czechoslovak Metrological Institute in Bratislava has prepared a set of following attested mono - element reference solutions: Al, Ag, As, B, Ba, Be, Bi, Ca, Cd, Co, Cr, Cu, Fe, Ga, In, K, Li, Mg, Mn, Mo, Na, Ni, P, Pb, Se, Sb, Sr, Sn, Te, Ti, V, Zn containing 1 000 ppm of the element in question in a precisely defined solution. The content of elements declared by the above mentioned Institute was attested on the basis of results obtained by methods of classical chemical analysis (gravimetry) and of atomic spectroscopy (atomic absorption spectrometry - flame and atomic emission spectrometry - flame and inductively coupled plasma). In the case of spectroscopic methods attested reference solutions of firms Alfa Ventron and Merck were used for calibration.

Five independent determinations were performed by classical chemical methods and 10 independent determinations by methods of atomic spectroscopy.

The obtained analytical results were statistically treated both, without taking in account the applied analytical method and with respect to the individual method.

Statistical parameters calculated for single elements (mean value, standard deviation and other) confirm the reliability of the declared content (1 000 ppm) and so the serious preparation of the investigated attested mono - element reference solutions.

On the basis of the performed analyses and statistical evaluation of their results, the prepared attested reference solutions can be declared as suitable for calibration and reference purposes.

COMPARISON OF DECOMPOSITION PROCEDURES FOR ARSENIC DETERMINATION IN BIOLOGICAL MATERIALS BY HYDRIDE GENERATION AAS

J. Száková[a], P. Mader, J.M. Bellama[b]
University of Agriculture, 165 21 Prague (Czechoslovakia)
[a]Agricultural Enterprise, 503 03 Smiřice (Czechoslovakia)
[b]Permanent address: Department of Chemistry, University of Maryland, College Park, MD 20742 (USA)

Decomposition of biological materials for arsenic determination by hydride generation AAS can be a problem because of high volatility of many arsenic compounds as well as the presence of the difficult to decompose organoarsenic compounds.

In this study three decomposition methods commonly used in analytical procedures were compared: **classical dry ashing** with the sample covered by a solid mixture of $Mg(NO_3)_2$ and MgO as an ashing aid; **wet digestion** in a mixture of HNO_3 + H_2O_2 + H_2SO_4 (5+5+1); and **dry ashing in a mixture of O_2 + O_3 + NO_x gases** (Dry Mineralizer Apion, Tessek, CSFR). Biological certified reference materials (CRMs) of different origin and different arsenic content (NIST 1577a Bovine liver, NIST 1572 Citrus leaves, BCR 278 Mussel tissue) and internal reference material (IRM) NSC-21 Industrial Compost Vitahum were used in this comparison.

Blanks obtained by classical dry ashing and wet digestion were found to be one order of magnitude higher than those from the Apion. For this reason it was impossible to determine the very low content of arsenic in the NIST 1577a CRM after decomposition by classical dry ashing and by wet digestion. Wet digestion also did not decompose the complex organoarsenicals (arsenobetaine) found in the CRM of marine origin (BCR 278). Results of the analysis of CRM NIST 1572 and IRM NSC-21 were comparable for all three methods studied.

Only dry ashing in the Apion seemed to be suitable for all four RMs studied. It was also found that recovery of As(III) and As(V) inorganic salts solutions spiked to the biological samples before decomposition was acceptable in the case of dry ashing in the Apion. Classical dry ashing and wet digestion can be used for samples containing more than 0,1 mg $As.kg^{-1}$ of dry matter because of the high detection limits for these analytical methods with the exception of marine biological samples, which were not decomposed by wet digestion.

A 38

COMPARISON OF PHOTOGRAPHIC AND PHOTOELECTRIC DETECTION FOR REE ANALYSIS BY ICP-AES

P.Šoltés, N. Pliešovská, Department of Chemistry, Faculty of Metalurgy, Technical University Košice, representative of the firm INULA

We have compared results, which were achieved during the REE analysis by ICP-AES. The signal registration was done through the optical system of the spectrograph PGS-2 on photographic plate WU-3, or the signal through the photoadapter (1,2) was registered with the aid ofthe register K 201. The work was mainly dedicated to two important parametres: - limit of detection
- precision

Values of the limit of detection achieved during the photoelectric detection are better in order than values achieved during photographic detection.

Values of precision are in order on the same level for both ways of detection. The signal in both cases was measured from newly prepared sample.

At the base of achieved results it can be stated, that despite more advantageous limits of detection, usage of the photographic registration has still its priority in cases of multielemental determination from the small volume of a sample.

(1) Koller L., ZN 50-53/88
(2) Sučik G., Konštrukcia fotoadaptéra (construction of the photographic adapter)

A 39

Determination of As, Bi, Sb, Se, Sn, Te and Hg by Hydride Generation and ICP/AES

L. Umanec, ITC-VÚK Panenské Břežany

Hydride generation and ICP/AES, as a step in determination of some elements in Groups IVA, VA and VIA has been valued because of its high sensitivity and relative simplicity.

The special spray chamber for hydride generation has been construted to decrease memory efect and to improve repeatability.

The optimal conditions for hydride generation and measurement by ICP/AES of As, Bi, Sb, Se, Sn, Te and Hg have been studied. Detection limits in µg/L level have been achieved. The conditions for the simultaneous determination of groups of elements have been established.

This analytical technique has been applied to the determination:
a) As, Bi, Sb, Sn and Se in drink and waste water
b) As, Sb and Bi in Pb (after separation)
c) As, Sb, Sn, Bi and Hg in sludge
d) Se in printer's paint
e) As, Sb, Sn and Bi in Cu-matrix.

A 40

GEOCHEMISTRY OF NORTH BOHEMIAN SULFUROUS COAL VERTICAL PROFIL

A. Vodičková, I. Sýkorová
Ústav geotechniky ČSAV, Praha

A profil of the anomalous seam part in the locality Černice (North Bohemian coalfield) intercepted by two boreholes was studied in detail. In accordance with chemical and petrographical analysis there are high-ash and high-sulfur coals. The occurrence of fine-grain forms of syngenetic Fe-disulfides disperged in coal matter is characteristic for both boreholes.

Trace elements (Cd, Co, Cr, Cu, Ni, Pb, Zn, As, Se), content of which is followed from the ecological point of view, were determined by flame AAS. To overcome the difficulties caused by bad capability of muffle furnace ashes from coals with fine disperged clay minerals and Fe-disulfides to be dissolved, ashing was performed by superoxidizing mixture (in device APION, t=360°C) and followed up by acid degradation in a pressure bomb (mixture HNO_3, $HClO_4$, HF, t=150°C).

The knowledge obtained indicates that coal of boreholes CN 138 and CN 20A is not able to be treated (lowering of sulfur content and toxic elements together) by obvious procedures and it is not suitable for practical use.

F 1

NEW DEVELOPMENT IN FTIR AND FT RAMAN SPECTROSCOPY

IVOR DOMINAK

NICODOM, Rep.Nicolet Instrument, Hlavní 2727, CS-141 00 Praha 4

ABSTRACT

Short introduction to FTIR and FT Raman spectroscopy.

Introducing of NICOLET FTIR spectrometers, like model 205 for routine analysis, dedicated analysers, 300-500-700 series instruments and top research instruments like 740, 800 or 910, the first stand-alone FT Raman spectrometer.

High-performance infrared microspectroscopy - special features of the Nic-Plan™ microscope, allowing to measure IR spectra of samples or their parts as small as $10 \mu m$

Sampling techniques - accessories, like diffuse reflectance /solid samples spectra without preparing KBr pellets/, grazing angle specular reflectance /thin layers/, horizontal ATR /strong absorbing samples e.g. liquids, polymers, water solutions/ etc.

Spectral libraries, SEARCH software - sophisticated method for identifying unknown samples.

Discussion.

Nic-Plan™ is a trademark of Nicolet Instrument Corporation.

F 2

Service of ARL spectrometers in Třinec Iron and Steelworks

Ing. Antonín Glos, Třinecké železárny, a. s., servis ARL

Since 1969 Třinec Iron and Steelworks performs the service activities for ARL - Applied Research Laboratories, Ecublens, Switzerland. The service concerns both optical emission spectrometers (ARL 3460, 3520, 3560, 3580 and Quantoport) and X-ray fluorescence spectrometers (ARL 8410, 8420, 8460, 8480, 8620, 8660, 8680).

Service center is situated in the building of the chemical laboratories of Třinec Iron and Steelworks, the consignement store is also there.

As the large number of ARL spectrometers was inslalled in Czechoslovakia, the second service center war established in Kladno i 1981.

The service ingeneers perform :

- consulting and publicity
- pre-instalation activity
- instalations of instruments
- repairs of instruments within warranty period
- repairs out of warranty period
- spare parts support
- trainning of the staff control and maintenance of instruments
- renovation of instruments

The new offer since 1992 is the lump service, wich includes preventive service visit at the customer twice a year free of charge. This visit covers cleaning of the electronic and the optics and adjustment of all parameters of the instrument. In the case of failure of the instrument the service ingeneers will come of the service visit with priority, not later then after 48 hours. All conditions of payment are specified in the service contract.

F 3

SETTING UP STANDARDS SUPPLIED BY 2 THETA

V. Helán

2 THETA, P.O.Box 103, 737 01 Česky Těšín

For compensation of long term nonstability (drift) of various analytical instruments (X-ray fluorescence spectrometers, optical *emission spectrometers with arc/spark or GDL or ICP excitation*, thermoevolution analysers and others) the setting up standards are used. The frequency of recalibration differs with the type of instrument and with the demands for the precission of analytical results. E.g. in metallurgical industry the typical interval of racalibration is 8 hours. To lower the time consumption of every recalibration special sets of setting up standards were developed.

Good setting up standard must fulfill following demands: proper concentrations of elements, as many of elements in one sample as possible but without interelement effects, good homogeneity, good stability in air (vacuum, under X-rays), good mechanical properties.

Glass and ceramics seem to be the best materials for the recalibration of XRF spectrometers. The universal set of 7 samples containing 46 elements was developed for various fields of application. For the cement industry special set of 4 samples containing typical 13 elements is offered.

Setting up standards of metals are produced in 3 versions: disc with polished surface for XRF, cylinders with grinded surface for the arc/spark and GDL OES and chips for ICP OES, AAS and other instruments working with solutions. The universal set of 7 samples for the analysis of steel, the samples of Ni-alloys and other non-ferrous metals are supplied.

For the recalibration and check of thermoevolution analysers for determination of carbon, sulphur, oxygen, nitrogen and hydrogen we have good oppinion with the metalic samples in the shape of pins, the use of which saves the time for weighting the samples.

Although setting up samples are the main stream, 2 THETA offers also other products:

- reference materials of steel, non-ferrous metals and silicates,
- environmental standards
- machines for sample preparation, e.g. pressing machine for preparation of pelets for XRF analysis, electric scissors for sampling of wires for the determination of C, S and gasses
- consumables and accesories for spectrometric laboratories, e.g. the holder for the analysis of wires on OES, brushes for cleaning electrodes, etc.

M 1

HOLE BURNING AS A POWERFUL TOOL FOR THE STUDY OF PHOTOPHYSICAL PROPERTIES OF PHTHALOCYANINE LANGMUIR-BLODGETT FILM

F. Adamec, M. Ambrož, E. Brynda*, J. Dian, M. Vácha and J. Hála

Department of Chemical Physics, Faculty of Mathematics & Physics, Charles University, Ke Karlovu 3, 121 16 Prague 2
*Institute of Macromolecular Chemistry ČSAV, Heyrovského nám. 2, 160 00 Prague 6, Czechoslovakia

Spectral hole burning is a low temperature technique eliminating inhomogeneous broadening of absorption and emission spectra. The measured persistent and/or transient spectral holes reflect the homogeneous line profiles and their widths are related to excited state relaxation times.

The persistent spectral hole burning method was applied to the study of photophysical properties of metal free tetra-tert-butyl phthalocyanine (Pc) Langmuir-Blodgett (LB) film are presented. Absorption and fluorescence spectra characterize the LB multilayers consisting of domains of well ordered molecules and of non-ordered molecules in off-domain positions. Homogeneous line profiles obtained from spectral holes in fluorescence excitation spectra (measured under short burning time limit) together with the temperature and burning wavelength dependence of the homogeneous linewidth are presented. In systems with high order and with tight molecular interactions (such as Pc LB films) excited state relaxation time is strongly influenced by fast intermolecular excited energy transfer from well-ordered domains to off-domain molecules. The fast energy tranfer is documented in the values of the excited state relaxation times (≈ 100 ps) and their temperature dependences (≈ $T^{1.15}$ law). The energy transfer efficiency in LB film artificial light harvesting antenna is approximately 5-10 times lower compared with natural photosynthetic antennae.

M 2

Photochromic properties of thiopyrans

Adamec M., Nešpůrek S., Kuthan J.[1], Šebek P.[1]

Institute of the Macromolecular Chemistry
Czechoslovak Academy os Sciences
162 06 Prague 6, Czechoslovakia
[1]Prague Institute of Chemical Technology
166 28 Prague 6, Czechoslovakia

Photochromic properties of 2,4,4,6-tetraaryl-4H-thiopyrans were studied. New optical absorption after the exposure to UV light was induced in the range 500-700 nm. Back reaction - the thermally activated bleaching process could be described by a stretched exponential (exp[t^{α}]). Interpretation of this behaviour in terms of dispersive relaxation phenomena was elaborated. The bleaching rate was a strong function of air oxygen - in vacuum the coloured form was stable for many days whereas on air the lifetime of the coloured form ca 1 hour was found. The possible mechanism of the photochromic reaction was suggested.

M 3

CZECHOSLOVAK *CW* TUNABLE TITAN SAPPHIRE LASER.

M. Ambrož, T. Polívka, *J. Kubelka and J. Hála

Department of Chemical Physics, Faculty of Mathematics & Physics, Charles University , Ke Karlovu 3, 121 16 Prague,
*Monokrystaly Turnov, 511 19 Turnov, Czechoslovakia

Construction and spectral parameters of a home-built tunable *cw* titan sapphire laser based entirely on Czechoslovak components are reported together with a typical example of NIR spectroscopical application.

The calculation of "Kogelnik" cavity parameters have been performed for 19 mm long rod of Ti^{3+} sapphire crystal cut with Brewster angle to optimize laser output power. Three sets of dielectric coated mirrors have enabled the laser generation in the spectral regions (700-760, 760-840 and 840-920 nm). The laser was tuned within the above mentioned spectral regions using a three plate birefringent filter inserted at Brewster's angle in the wing of the laser resonator. Typical spectral width of the laser emission was ≈ 1 cm^{-1}. Further spectral narrowing (≈ 0.1 cm^{-1}) can be achieved by placing a thin Fabry-Perot etalon in the laser cavity. Mean laser output power ranged in hundreds of miliwatts (near 790 nm) for ≈ 10 W Ar-ion laser multiline optical pumping. The laser threshold was found between 3 and 4 W. Use of water cooled crystal as a lasing medium is advantageous over laser dyes for NIR region due to its stability and long term cost effectiveness.

The Ti^{3+} sapphire *cw* tunable laser will find promising applications in many areas of near infrared spectroscopy (e.g. hole burning of photosynthetic bacteria, spectroscopy of GaAs and rare earth ions) and for photodynamic therapy of malignant tumors (using deep red absorbing sensitisers reduces the risk of an undesirable laser light action on treated tissue).

M 4

A NEW METHOD FOR LINE ASSIGNMENT IN OVERCROWDED NMR SPECTRA

V. Blechta * J. Pelnař ⁑ J.Schraml *

* Czechoslovak Academy of Sciences,
Institute of Chemical Process Fundamentals,
165 02 Praha 6 - Suchdol, Czechoslovakia
⁑ Czechoslovak Academy of Sciences,
Institute of Organic Chemistry and Biochemistry,
Fleming sq. 2, Praha 6 - Dejvice, Czechoslovakia

The proposed pulse sequence is designed for samples, with overlapping signals from several ^1H spin systems (e.g. signal belonging to different components in a mixture or to different parts of a large molecule which are not coupled). In such cases the overlap prevents assignment of ^{13}C NMR lines. For spin systems, which have one or more proton NMR lines well separated from all the others, we can by the sequence selectively excite such separated line of one particular system. The excited magnetization is transferred by the isotropic mixing to all protons of the selected system in the first step and to attached carbons by INEPT pulse sequence in the second step. Carbon signal is acquired. The proposed sequence is:

soft(90,^{1}H)-TOCSY(^{1}H)-INEPT(^{1}H,^{13}C)-acquire(^{13}C)

Pulse sequence is demonstrated on the sample of amikacin.

M 5

NORMAL COORDINATE ANALYSIS AND ASSIGNMENT OF VIBRATIONAL FREQUENCES OF SULFUR YLIDES

Igor E.Boldeskul
Institute of Organic Chemistry Ukrainian Academy of Sciences
252660 Kiev 94, Ukraine

Identification of frequences of Element (E)-Carbon E=C formally double bond, characterized by a considerable contribution of $\overset{+}{E} - \overset{-}{C}$ canonic structure, often presents difficulties in establishing spectra-structural correlations for ylide molecules and zwitter-ions.

Experimental studies and spectra calculations of some sulfur ylides $Me_2S=CR_2$ (R=C≡N, COR) and of malononitrile carbanion demonstrate splitting of stretching frequences of geminal functional groups, caused by their vibrational interactions, whose value depends on extra charge delocalization character in the carbanionic fragment as well as on sulfonium centre participation in the latter. Vibrational splitting value of indicator absorption bands of geminal substituents in a mesomer type carbanionic fragment is usually higher in comparison to the groups, not involved in the conjugation.

Vibration of the ylide bond is not characteristic in frequency and its force constant is of an average value between single and double sulfur-carbon bond.

GENERATION AND LOW TEMPERATURE SPECTROSCOPY OF CLUSTERS AND OTHER TRANSIENT MOLECULES

V.E.Bondybey

Institut für Theoretische und Physikalische Chemie
Technische Universität München, Garching

The generation of free radicals, molecular ions, metal clusters and similar transient molecules usually occurs in energy rich environment, such as plasmas, discharges or high temperature furnaces. Spectroscopic characterization, on the other hand, is greatly facilitated at low temperatures. A key to successful characterization of clusters and other reactive intermediates is therefore development of low temperature techniques for their generation.

One such technique developed in our laboratory involves pulsed laser vaporization of metals and other solid samples in the presence of cold carrier gas, followed by laser induced characterization of the products. Another technique useful for transient generation combines electric discharge adiabatic expansion cooling of the produced species.

Matrix isolation spectroscopy offers an alternative to gas phase jet techniques for studies of reactive species. By freezing the molecules of interest at 4-10 K with a large excess of inert gas they can be accumulated for subsequent leisurely study by a variety of spectroscopic techniques.

We will discuss a number of examples of application of such low temperature techniques for a variety of systems. These range from simple metal dimers of theoretical interest such as LiBe or Al_2, over molecular ions, to free radicals of importance in the atmosphere, including halocarbenes, as well as the CNN radical and similar species.

M 7

STUDY OF $BaTiO_3$ CERAMICS BY X-RAY MICROANALYSIS AND IR SPECTROSCOPY

J. Briančin, L. Medvecký, J. Mihalik, K. Havrilová,
K. Ďurišinová

Inst. of Experimental Metallurgy, Slovak Academy of Sciences, Košice, Czechoslovakia

The paper is intended to study electroceramics based on the doped form of $BaTiO_3$ - orientated at the practical utilization of PTC effect. The elements Sb and Nb in the form of oxides (0.3 mol%) were used as dopants. Liquid forming additivies Al_2O_3 and SiO_2 were used in the stage of high temperature sintering of compacted powdereds $BaTiO_3$ phase for the purpose of activation of recrystallization process.

The final electric properties of electroceramics reflect its recrystallized structure.

The X-ray microanalytic studies have been carried out to evaluate the influence of additivies on recrystalizatio processes and their resultant distribution within the recrystallized structural grain.

IR spectrometry represented the fundamental evaluation method of the quality of preparation of the basic powdered $BaTiO_3$ phase by the high temperature reaction of homogenized starting components ($BaCO_3$, TiO_2 or PbO).

Results of X-ray microanalysis and IR spectroscopy are faced with the obtained electrical properties of final doped $BaTiO_3$ ceramics represented by resistance-thermal characteristics.

M 8

SYNTHETIC POLYPEPTIDES AS ADSORBATES AND MOLECULAR SPACERS FOR PORPHYRINS : A SURFACE ENHANCED RAMAN SCATTERING STUDY

K. Čermáková*[1,2], P. Matějka[1], P. Pančoška[2], V. Baumruk [3]and B. Vlčková[1]

[1]Dept. of Physical and Macromolecular Chemistry, Charles University,
Hlavova 2030, CS 128 40 Prague 2, Czechoslovakia
[2]Dept. of Chemical Physics, Charles University
[3]Institute of Physics, Charles University

Investigation of biomolecules represents one of the most challenging applications of Surface Enhanced Raman Scattering (SERS) spectroscopy. For obtaining relevant information from the SERS spectrum of a biomolecule, two questions have to be answered: (1) does the SERS spectrum provide information about the entire molecule, or only about the part of biomolecule which is in a close vicinity of the metal surface? and (2) is the native structure of biomolecule altered upon adsorption via chemical interaction with the metal surface? As a first step to answering these questions for large biomolecules, e.g. proteins, chemically more simple species are usually investigated.

In this study, SERS spectra of a series of lysin-containing synthetic polypeptides : KA, KAA, KAAA, KGG, KLA (K=lysin, A=alanin, G=glycin, L=leucin, average degree of polymerization ca. 30) and polylysin have been investigated in the *Ag colloid/polypeptide* systems. Generally, the SERS spectra of all polypeptides studied show rather weak, broad bands attributable to amide I-VI. The band possitions correspond to those observed in normal Raman spectra of polypeptides in aqueous solution. The broad band at ~1635cm^{-1} which also has its counterpart in the normal Raman spectra is assigned to H_2O molecules associated with the polypeptide chains. However, for KAA and KAAA, also a different type of SERS spectra have been observed. These are characterized by strong, narrow bands of amide I-VI, the maxima of which are shifted and/or split into a doublet with respect to those in the normal Raman spectra. While the former, more general type of SERS spectrum indicates physisorption of polypeptide, the latter is attributed to the species chemisorbed on Ag colloidal surface.

Lysin-containing polypeptides are known to form ionic complexes with TPPC4 (5,10,15,20-tetrakis(4-carboxyphenyl)porphyrin) via interaction of $-NH_3^+$ groups of lysins with the COO^- groups of the porphyrin [1]. To test the ability of polypeptides in adsorbed state to interact with the porphyrin, free base TPPC4 was added to the *Ag colloid/polypeptide* SERS-active system. The newly formed *Ag colloid/polypeptide/TPPC4* system provides a high quality SE(R)RS (R=resonance) spectrum of the free base form of the porphyrin. This is in a sharp contrast to the SER(R)S spectrum of *Ag colloid/TPPC4 system*, in which entirely the bands of the metalated Ag(II)TPPC4 species have been observed [2]. In the *Ag colloid/polypeptide/TPPC4* system, the polypeptide appears to play the role of a molecular spacer between the porphyrin and the Ag surface. Owing to the polypeptide-porphyrin interaction, TPPC4 molecules are attracted to the vicinity of the surface while, simultaneously, are prevented from a direct chemical interaction with the Ag surface. Interestingly, both the physisorbed and the chemisorbed polypeptides show a comparable efficiency as molecular spacer.

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M 9

INSPECTION OF THE 900-700 cm^{-1} REGION IN THE FTIR SPECTRA OF COAL TARS.

J. Černý, Institute of Geotechnics CSAS, Prague 8

The FTIR spectroscopy is an excellent tool for an assessment of the chemical composition of solid and insoluble fuels, especially coals.It is also the only routine analytical method available for the determination of hydrogen distribution in such materials.

The evaluation of out-of-plane vibrations in the 900-700 cm^{-1} region is one of two posibilities to assess the aromatic hydrogen concentration on a quantitative basis. Except the response of aromatic CH bonds, this region is also known to have some contribution of minerals and methylene rocking modes. To examine the appearance and position of the aliphatic bands, the FTIR spectra of coal-tar aromatics in this region were compared with the hydrogen distribution measured by ^{1}H NMR spectroscopy.

The FTIR spectra were processed by using curve-fitting and self-deconvolution procedure. At least 14 bands were resolved for mono and diaromatics and 11 for higher aromatics. Among them only two bands near 791 cm^{-1} and 784 cm^{-1} can be with some certainity assigned to aliphatic CH bonds. They were resolved in the spectra of mono- and diaromatics only, and their average proportion of the whole 900-700 cm^{-1} area was about 8 per cent. The 835 cm^{-1} band, considered as the aliphatic band, did not possess any definite trend with hydrogen aromaticity. The integral intensity of the 720 cm^{-1} band raised with hydrogen aromaticity and, simultaneously, decreased with increasing methylene concentration. Although this band is well known as the aliphatic band of long chain methylene, the results obtained are indicative of some aromatic CH contribution to the 720 cm^{-1} band, as an abundance of long chain aliphatic substituents is hardly to expect in tar aromatics.

M 10

HOLE BURNING SPECTROSCOPY OF NATURAL PORPHYRINS.

J. Dian, F. Adamec, M. Ambrož, J. Pšenčik, M. Vácha and J. Hála

Department of Chemical Physics, Faculty of Mathematics & Physics, Charles University, Ke Karlovu 3, 121 16 Prague, Czechoslovakia.

Uroporhyrins, together with other natural porphyrins, are important intermediates occurring in the metabolic pathway to protoheme. They are important indicators of pathogenic states in an organism. Conventional techniques of the optical spectroscopy provide only low-resolved absorption or luminescence spectra due to the inhomogeneous broadening. Low temperature spectroscopy makes possible to eliminate the inhomogeneous broadening and to determine various molecular parameters such as homogeneous linewidth of the optical transition, electron-phonon coupling, etc.

Low temperature hole-burning spectra of uroporphyrin I esters (octamethylester - MeUP, octaethylester - EtUP and octa- (n-propyl)-ester - PrUP) in amorphous ($CHCl_3$) matrix are presented. The hole-burning spectra were excited by *cw* ring dye laser within the region of the 0-0 transition and measured in temperature range 1.7-20 K. The homogeneous linewidths were determined from the dependence of the holewidth on burning time and intensity (fluence). The temperature dependence of the homogeneous linewidth Γ_{hom} follows the T^a dependence as it is expected for the amorphous systems.

M 11

STRUCTURAL AND LUMINESCENCE PROPERTIES OF ZnS PREPARED BY SHS

Dvořák L., Kubínek R., Kupka Z., Mašláň M.
(Palacky University, Olomouc)

Rusek J.
(Institute of mineral raw materials, Kutná Hora)

Polycrystallic samples of ZnS were studied by light and electron microscopy, the analyse of the characteristic x-ray, and the measurement of photoluminescence spectra.

Pure or with the activator (Mn, Ba, Y - 0,5 mol %) starting powdered components (Zn ,S) were pressed after the perfect homogenization. The cylinder (diameter 30 mm, height from 50 to 300 mm) was placed to the reactor where is evoked thy synthesis by local Joule heating. Synthetized samples are created pollycrystalic ZnS (97%) with superiority of sphaleritic phase (a= 0,5417 nm) and less suplly of wurtzit phase (a= 0,3826 nm, c= 0,6271 nm).

Three characteristic zones with different distribution of activator was observed in cross-section by light and electron microscopy. Weight concentration of Zn and S in all of three zones was determined by the analyse of characteristic X-ray. Maximum intensity of the broad band photoluminescence of the self-activated ZnS is at about 515 nm, in ZnS--Mn is about 580 nm in ZnS-Ba is important deposit of emission of maximum at about 475 nm. The interpretation of luminescence emission can be: in case of ZnS-Mn there is non-recombination type of the luminescence, in other cases there are recombination type.

LASER INDUCED FLUORESCENCE AS A SENSITIVE INSTRUMENT OF MEASUREMENT BIOLOGICAL ACTIVITY OF CONIFERS

P.Gavrilov, A.Jančárek, V.Krajíček, J.Nováková
and M.Vrbová

Faculty of Nuclear Science and Physical Engineering
Technical University of Prague,
Břehová 7, 115 19 Praha 1, Czechoslovakia.

We describe experimental arrangement for laser induced fluorescence (LIF) of biological objects study, calibration of instrumental constants and we estimate absolute value of number photons received from biological objects. We find an instrumental requirements for using of laser induced fluorescence in remote investigation of biological activity and ecological damages of the conifers.

Our measurements show, that laser induced fluorescence spectrum is very sensitive to vegetative period, temperature and the time breaking off the twig before measurement. Observable difference in the spectrum we find during half an hour after breaking off the twig from the tree. We try to find the method of calibration and comparatione of various samples for quantitative analyze.

In our experiments we used XeCl excimer laser (308 nm) with energy 100 mJ in ten nanosecond pulse fired with repetition rate up to 50 Hz. Comparison of spectrum measurements results on energy density of the laser pulse we made, too. The spectral analysis was done by a dual grating spectrometer equipped with a photomultiplier (with S20 photocathode). It is known [1], [2] that the fluorescent spectra of conifers induced by ultraviolet pulses and measured in the spectral range from 350 to 800 nm show three broad peaks at 450, 540 and 740 nm. All experiments were full controlled by PC computer.

The energetical efficiency on a different wavelengths dependance we calculate from comparison with radiation of black body, He-Ne laser and from numerical aperture of spectrometer. From this calibrations we can extrapolate sensitivity of other experimental arrangements and projects of biological object remote investigation by laser induced fluorescence.

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M 13

SOFTWARE FOR REMOTE MODE OPERATION OF INFRARED SPECTROPHOTOMETER SPECORD M80 FROM AN IBM COMPATIBLE PERSONAL COMPUTER

Vladimír Glaser and Karel Volka
Department of Analytical Chemistry
Institute of Chemical Technology
CS-166 28 Praha 6, Czechoslovakia

Software for remote mode operation (written in Turbo Pascal) of infrared spectrophotometer SPECORD M80 (C. Zeiss, Jena) completed with optional Computer Handling Card and communication port with RS 232C interface supplied by manufacturer is described.

The primarily task of the software is data collection and data storage on hard or floppy disc. Software menu mode allows to initiate all commands and set parameters by selecting the commands and parameters from pop-up menus using either the mouse or the keyboard. Also collection or transfer of correction values is possible. The collected data are stored in temporary storage area, displayed on the screen or printed, and stored in ASCI, XY or M80 code. Conversion programs to IRD format used in NICOLET PC/IR software and DIF format used in LOTUS, RS/1, VISICALC, etc. are also included.

An IBM compatible PC with one floppy disc unit and operational memory min. 512 kB is needed (AT 286/16, HD 40 MB, VGA and Mouse are recommended).

M 14

THE INTERACTION OF KIESELGUHR AND BASIC NICKEL CARBONATE (HYDROGENATION CATALYST PRECURSOR) BY MEANS OF IR SPECTROSCOPY.

F. Hanousek, E. Večerníková, V. Zapletal

Institute of Inorganic Chemistry, Czechoslovak Academy of Sciences
250 68 Řež near Prague.

The reaction conditions of the preparation of the nickel catalyst precursor (basic nickel carbonate on kieselguhr support) have the main influence on the activity and selectivity of the resulting catalyst. The interpretation of the IR spectra of the precursor samples prepared with varied ratios of Na_2CO_3 / $NiSO_4$ give the evidence by the strong interaction between Ni-O bonds of the precursor and Si-O bonds of the support. This effect is demonstrated preferably by the Si-O antisymetric stretching vibrations which are shifted from a broad unresolved band in pure support at 1093 cm^{-1} to a well resolved doublet at 990 and 1050 cm^{-1} . The intensities (after numerical separation) of these bands are characteristic for different types of interactions and dependent on the condition of the precipitation of nickel salts with an alkali. Thus, can be obtained silicates of garnierite (Ni-antigorite) or pimelite (Ni-montmorillonite) types. These phases show high resistance to reduction of the precursor to the catalytic active metal under general condition employed for nickel catalyst activation (i.e. 400° C).

M 15

DIFFERENCES IN THE CELL HYDROPHOBICITY BETWEEN TWO *PSEUDOMONAS* STRAINS. A SPECTROPHOTOMETRIC STUDY.

E.Horská, M.Labajová, W.Ziegler, J.Pokorný
Inst. of Ecobiology, Slovak Acad. Sci., Bratislava, ČSFR

Hydrophobic interactions are considered to play an important role in a variety of microbial phenomena, as adhesion, phagocytosis, growth on insoluble substrates, and gliding. Components improving (hydrophobines) or reducing (hydrophilines) the hydrophobicity of the microbial cell surface might well coexists on the outer membrane of the bacterial cell.

Our study deals with hydrophobic properties of *Pseudomonas putida*, and *Pseudomonas fluorescens*, which were evaluated on the base of the bacterial adherance to hexadecane and by a simple spectrophotometric method described by Rosenberg (1986). The results of these experiments show that *Pseudomonas fluorescens* compared with *Pseudomonas putida* displayes a better adherance to hexadecane as well as to diesel oil. This proofs the stronger hydrophobicity of the outer surface of *Pseudomonas fluorescens*.

In a further approach we have studied the transport of the lipophilic dye Gentian Violet into the cells of both bacterial strains. In the case of *Pseudomonas putida* only a weak influx was observed. Different from this behavior *Pseudomonas fluorescens* showed a fast and strong uptake of this dye. In both cases the influx could be inhibited by sodium azide as well as by potassium cyanide.

As known from literature lipopolysaccharides constitute the main penetration barrier against Gentian Violet. Additional contibutions come from murein and mayby from some other components of the outer bacterial membrane. We assume these components constituting the penetration barrier against Gentian Violet to be the reason for the different hydophobicity of the outer membrane of *Pseudomonas putida* and *Pseudomonas fluorescens*. An exact proof of this hypothesis requires however additional experiments.

M 16

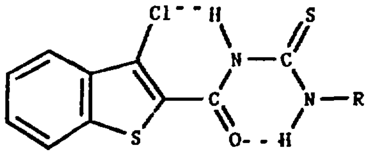
STRUCTURE AND INTRAMOLECULAR HYDROGEN BONDING OF N-AROYL-N'-MONOSUBSTITUTED DERIVATIVES OF THIOUREA

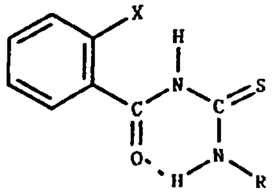
O. HRITZOVÁ, G. SUCHÁR, I. DANIHEL

Department of Organic Chemistry, Faculty of Natural Sciences,
P. J. Šafárik University, Košice, ČSFR

It is known that hydrogen bonds can affect a number of various properties of organic compounds,and the knowledge of nature of hydrogen bond can be utilized for prediction of structure, reactivity and stereochemistry of these substances.

In the present contribution are summarized results obtained for geometry and electronic structure of conformers in derivatives of N-(3-chloro-2-benzo-[b]thienocarbonyl)-N'- monosubstituted thiourea, resp. in derivatives of N-substituted N'-benzoyl- and N'-(2-chloro- benzoyl)thiourea, to be studied their intramolecular hydrogen bonds. In order to solve this problem, we compared the results of calculation on the basis of molecular dynamics with experimental values of IR spectra of mentioned thioureas. We found that the atomic distances *of the functional groups entering to hydrogen bonds, and torsion angles of* -CO-NH-CS-NH- arrangement obtained in this way are suitable to estimate for formation of intramolecular hydrogen bonds.





X = H, Cl

R = C_2H_5, C_6H_5

M 17

ACTIVE FUNCTIONAL AND PASSIVE STRUCTURAL CHANGES IN FLUORESCENCE SPECTRUM OF CHLOROPHYLL A IN VIVO

P. Ilík, J. Nauš, R. Kuropatwa, T. Klinkovský
(Department of Experimental Physics, Palacky University,
tř. Svobody 26, 771 46 Olomouc, Czechoslovakia)

Fluorescence spectrum of chlorophyll a in green leaves reflects structural and functional state of the leaf assimilation tissue in a complex manner. The heterogenous structure and pigment composition of the tissue causes distortion of the spectrum shape mainly by fluorescence reabsorption, light scattering, light reflection and deviation from the exponential absorption law. The functional changes are both at room temperature and at 77 K documented by relation of photosystem II (PS II) and photosystem I (PS I) emissions.

In order to estimate the degree of passive distortions in the fluorescence spectrum, both experimental approaches and model calculations have been used. As a typical functional change, the effect of photoinhibition on the room temperature and 77 K fluorescence spectrum has been studied. A reversible decrease of PS II emission (F-685 and F-695 bands) by about 30 % with respect to PS I emission (F-735) was found under constant structural parameters and chlorophyll content. The change in emission is interpreted as an enhanced fluorescence quenching in PS II antennae due to protective dissipative deactivation of excited states by zeaxanthin, a component of the reversible xanthophyll cycle. A relation between photoinhibition and photobleaching is discussed.

M 18

A SIMPLE ADAPTATION OF A SPECTROPHOTOMETER FOR CHEMOTAXIC STUDIES

T.Kmeť, J.Pokorný, E.Horská, W.Ziegler, M.Labajová,
A.Brunovská
Inst. of Ecobiology, Slovak Acad. Sci., Bratislava, ČSFR

Motile organisms are attracted by certain chemicals and repelled by others - positive and negative chemotaxis. Since the 1960s bacterial chemotaxis hase become a subject of wide research. Several different methods have been developed to study and to examine this phenomen. Most of them however are expensive and experimentally hard to handle.

We have modified the kyvette holder in our spectrophotometer by adapting a micrometer drive to it which allows a controlled shift of the sample kyvette in an up/down direction. In this way it was possible to monitore time dependent changes in the distribution of bacteria by their optical density inside the kyvette.

With this simple arrangement we were able to show how *Escheria coli* bacteria respond to a substrate gradient maintained in the kyvette by immobilization of glucose.

M 19

URINARY CALCULI ANALYSIS BY MEANS OF INFRARED SPECTROMETRY AND FTIR SPECTROMETRY

M. Linhartová, Geological Survey Brno
V. Machovič, Institute for Geotechnics Academy of Sciences Praha

Analysis of urinary concrements has a very important place in clinical biochemistry departments, as it is one of the basic prerequisites for effective causal therapy and prophylaxis of neprohrolithiasis. Qualitative chemical reactions, used most frequently, have shortcomings as regards the identification of components of calculi. An accurate identification can be made only by physical methods, which, however, call for very expensive equipment. Clinical departments in Prague and Brno cooperate therefore with research institutes which possess the necessary equipment and where the analyses of calculi are made. Because the majority of clinical biochemical departments have limitied access to modern infrared computer controlled spectrometers, this form of cooperation was used also in the authors' department. The spectra were measured on infrared disperse spectrometry Perkin Elmer 783 with the data station 3 600 and FTIR Bruker IFS 88.

M 20

RELATIVE SIGNS OF $J(^{119}Sn,^{13}C)$ $J(^{119}Sn,H)$ AND $J(^{13}C,H)$ COUPLING CONSTANTS IN SOME ORGANOTIN(IV) COMPOUNDS USING 2D NMR

A. Lyčka[a], J. Jirman[a], J. Holeček[b], I. Tkáč[c]

[a]Research Institute of Organic Syntheses, 532 18 Pardubice-Rybitvi

[b]Department of General and Inorganic Chemistry, Institute of Chemical Technology, 532 10 Pardubice

[c]Institute of Inorganic Chemistry, Slovak Academy of Sciences, 842 36 Bratislava

Two-dimensional H,C-COSY spectra of some tetra-, penta- and hexa-coordinated organotin(IV) compounds were measured. The relative signs of $J(^{119}Sn,^{13}C)$ and $J(^{119}Sn,H)$ coupling constants were determined after analysis of the orientation of the appropriate $^{119/117}Sn$ satellites in the H,C-COSY spectra. If the high-frequency tin satellite in the ^{13}C dimension correlates with the high-frequency tin satellite in the ^{1}H dimension the signs of $^{n}J(^{119}Sn,^{13}C)$ and $^{(n+1)}J(^{119}Sn,H)$ are the same. The relative signs in Bu_nSn and Bz_nSn (n = 2,3) derivatives are opposite, whereas in Ph_3Sn derivatives these signs are the same for carbon atoms in the ortho and meta positions and opposite for carbon atoms in the para positions. In Sn,H-COSY spectra, carbons act as "passive" nuclei and these measurements enable to determine the relative signs of $J(^{119}Sn,^{13}C)$ vs. $J(^{13}C,H)$.

M 21

DIFFUSE REFLECTANCE FOURIER TRANSFORM INFRARED SPECTROSCOPY IN THE ANALYSIS OF COAL OXIDATION

V. Machovič, B. Taraba*, H. Pavlíková, E. Šebestová, A. Vodičková

Institute of Geotechnics CSAS, Prague 8

*Mining Institute CSAS, Ostrava

Diffuse reflectance Fourier transform infrared spectroscopy (DRIFT) has been used as a method for monitoring of chemical structural changes during oxidation of coal. The DRIFT spectroscopy enables fast and sensitive judgement of susceptibility of coal to oxidation in seams or in artificial oxidation of coal on a laboratory scale. This technique does not require a supporting matrix which can contain artifacts and enables measuring of the infrared spectra only with minor sample preparation.

By DRIFT spectroscopy it was found that subbituminous coals with various oxireactivity differ considerably in the content of oxygen functional groups such as ketones, carboxylic acids and anhydrides. The DRIFT oxidation indexes of coals determined by the "carbonyl" to "aliphatic" ratio exhibited similar trend as spontaneous combustion characteristics.

DRIFT spectra were also suggested as an effective way of predicting the degree of the postsedimentary oxidative alternation of bituminous coals (so called "dead coals") from Ostrava basin.

M 22

THE ROLE OF TRITON X-100 AS MOLECULAR SPACER FOR SERS SPECTROSCOPY

P. Matějka[1*], J. Vohlídal[1], V. Baumruk [2]and B. Vlčková[1]

[1]Dept. of Physical Chemistry, Charles University, Hlavova 2030,
CS 128 40 Prague 2, Czechoslovakia

[2]Institute of Physics, Charles University, Czechoslovakia

The SERS-active Ag silver surfaces possess several typical features. One of the characteristics is the presence of reactive Ag_n^+ species (n>1) which is responsible for the chemical interaction of various types of adsorbates with the surface [1,2]. The information about the native form of the adsorbate is distorted, as the molecular structure is altered by chemisorption. The information about the native, unaltered form can be obtained by the choice of an appropriate spacer, which: would: (i) prevent chemisorption of the adsorbate and (ii) ensure the fixation of the adsorbate onto the spacer-modified Ag surface in such a way that the adsorbate experiences the surface enhancement of Raman scattering [2]. The attention is focussed on a non-ionic surfactant Triton X-100 in this study. Triton X-100 consists of the hydrophilic poly(oxyethylene) chain and the p-(1,1,3,3-tetramethylbutyl)-phenyl group forming the hydrophobic part. The idea is that while one part of the surfactant could interact with Ag surface, the other one could be exposed to an interaction with the adsorbate studied. The results of the study of Triton X-100 adsorption on Ag colloidal surface showed that while the hydrophilic part is chemisorbed, the hydrophobic part is not in contact with Ag surface [2]. These results indicate that the hydrophobic non-adsorbed part can interact with another species.

For investigation of the ability of Triton X-100 to act as an molecular spacer we selected the water soluble free base 5,10,15,20-tetrakis(4-carboxyphenyl)porphyrin (TPPC4) and its silver metalated analogue (Ag(II)TPPC4). The free base TPPC4 is chemisorbed on the colloidal Ag surface as Ag(II)TPPC4 surface complex [1], while the synthetically prepared Ag(II)TPPC4 can be hardly adsorbed directly on the Ag surface. On the other hand, high quality SERS spectra of both TPPC4 and Ag(II)TPPC4 native species are obtained on the Triton X-100 modified Ag surface. To elucidate the role of the hydrophobic part of surfactant for obtaining high quality porphyrin spectra on spacer modified surface we studied SERS-active systems with surface modified by Polyethyleneglycol (PEG) 400, which represents a model of the hydrophilic part of Triton X-100. The SERS spectra of systems Ag colloid/Triton X-100/TPPC4 (A) and Ag colloid/PEG 400/TPPC4 (B) are in a sharp contrast. The marker bands of TPPC4 are more than 10 times as intense in spectrum A than in spectrum B although the same amount of porphyrin is present in both systems. This comparison demonstrates the key role of hydrophobic part of surfactant in localizing sufficient amount of TPPC4 molecules to the vicinity of the Ag surface. The attraction of TPPC4 originates from hydrophobic interaction between the porphyrin macrocycle and the hydrophobic part of Triton X-100. The same kind of interaction is responsible for fixation of Ag(II)TPPC4 (*synth.*) on the Triton X-100 modified Ag surface.

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M 23

THE SPECTROPHOTOMETRIC STUDY OF THE INTERACTIONS OF TENSIDES WITH VARIOUS TYPES OF ORGANIC DYES

I.Němcová, L.Čermáková
Department of Analytical Chemistry, Charles University, Prague

Sulphophtaleines and azo dyes are the most frequently used organic dyes for spectrophotometric determinations and also for volumetric and neutralization titrations. Some properties of these dyes are strongly affected by surfactants (tensides). Thus, the effect of cationic tenside (Septonex) and anionic tenside (sodium dodecylsulphate) on the absorption spectra and dissociation of triphenylmethane dye Pyrocatechol Violet, xanthene dye Brompyrogallol Red and azo dye Calconalide I was studied. As the interaction of dyes with tensides is strongly affected by the salts present, the effect of the ionic strength was also studied.

It was found that the changes in the absorption spectra of the individual dissociated forms of dyes are mainly a result of influences of the tenside on the dye dissociation. The shift of dissociation constants is determined by the type and the concentration of the tenside and also by the concentration of salts. In the case of Calconalide I, the equilibrium between the tautomeric forms is also influenced.

M 24

^{13}C CP/MAS NMR, EPR AND IR STUDIES OF BURIED WOOD

H. Pavlíková, E. Šebestová, J. Černý, V. Machovič, I. Sýkorová
Institute of Geotechnics, Prague 8

Chemical structure of the buried wood from the middle course of the Labe river valley was determined by solid state nuclear magnetic resonance, electron paramagnetic resonance and Fourier transform infrared spectroscopies.

With the increasing degree of gelification the peaks of cellulose gradually diminish from the NMR spectrum whereas the concentration of lignin components increases. The main indicators of such changes are the peaks of methoxyl groups at about 56 ppm and peaks in the area of aromatic carbons. In accordance with these changes during gelification, the EPR spectra also show the increasing concentration of free radicals. In the FTIR spectra, the ratio of methyl and methylene bands near 2877 cm^{-1} and 2840 cm^{-1} can be taken as a suitable indicator for the estimation of the degree of gelification.

An acid hydrolysis using concentrated hydrochloric acid was carried out on one of the least gelified wood with the lowest ash content to simulate the gelification process. The structural changes were analyzed by the above mentioned spectroscopic methods.

M 25

CATION ADSORPTION ON OUTER BACTERIAL MEMBRANE EVALUATED FROM SPECTRAL CHANGE OF METYLENE BLUE

J.Pokorný, E.Horská, M.Labajová, W.Ziegler, A.Brunovská
Inst. of Ecobiology, Slovak Acad. Sci., Bratislava, ČSFR

Methylene Blue (MB) is a positively charged probe. When added to a suspension of *Pseudomonas putida* the dye binds electrostaticly to the outer bacterial membrane. It forms there dimeres which have in the neighborhood of negative charges on the membrane surface a smaller molar extinction coefficient. As a result the absorbance of MB decreases. When cations are added to the system MB is partially released and the adsorbance starts to increase again.

Based on this effect we have examined the adsorption of different cations by the outer membrane of *Pseudomonas putida*.

The effect of different cations added to the bacterial suspension to make the same final concentration on the adsorbance increase was in following order:

$$Al^{3+} > Cd^{2+} > Mg^{2+} > Ca^{2+} > Na^{+} > (C_2H_5)_4N^{+}$$

As mentioned above the extent of the adsorbance increase is a measure for the strength the cations are bound to the negatively charged bacterial membrane.

In the absence of a specific adsorption the double layer theory predicts that cations of same charge should impose identical effects on the surface potential of the bacterial membrane. Identically increased optical adsorbances should therefor expected in the case of all equal charged cations as long as their final concentrations in the suspension are the same. The fact that the effects of Cd^{2+}, Mg^{2+}, and Ca^{2+} are different let us assume that on the outer bacterial membrane a specific adsorption of cations occures.

M 26

Emission of Plasma Induced by XeCl or ArF Excimer Laser on Silicon Surface

J. Polecha, A. Luches*, M. L. De Giorgi*, A. Perrone*, J. Polan
Institute of Physics, Czechoslovak Academy of Sciences, Prague
* University Lecce, Department of Physics, Lecce, Italy

Laser induced plasma is a source of particles (for deposition) and a source of radiation (from infrared to soft X-ray region). During ablation, both clusters (with dimensions of order of μm) and individual atoms and ions are evaporated [1].

We present both time-resolved and time-integrated spectra of plasma emission induced by excimer lasers (either ArF with $\lambda = 193$ nm or XeCl with $\lambda = 308$ nm) on single crystal silicon surface (100). Laser beam was focused to overcome ablation threshold (1.6 Jcm^{-2}). The time-integrated spectra of plasma emission were recorded on Polaroid film and the time-resolved spectra were measured by means of photodiode (rise time 3 ns).

In the time-resolved spectra the two lines at 386 nm and 413 nm, both belonging to Si II, were dominating. In time integrated spectra, intensive line at 391 nm (ascribed to Si I) appeared with intensity practically independent on laser beam fluence. In the interval 3.2 Jcm^{-2} — 4.1 Jcm^{-2}, the intensities of Si II lines increased in time-integrated measurements with increasing energy density in contrary to [2]. Because of the remarkably slower increase of Si I line intensity (in time scale) in comparison to that of Si II the emission of which prevailed during plasma emission (from the onset of laser pulse to the beginning of emission decay), it has been reasonable to suppose that the Si$^+$ ions were the primary energy carriers.

Knowing tabulated values of excitation energy of lines above mentioned, namely, 12.8 eV (for 413 nm), 10.1 eV (for 386 nm), and 5.1 eV (for 391 nm) one can directly obtain Si$^+$ ions energy. These values agreed quite well with average speed values (in plasma expansion direction) measured either by means of probe beam deflection [3] or mechanical shutter.[1]

It was proved that there was sufficient part of individual Si$^+$ ions in plasma plume and that their energy was close to energy of chemical bonds. It was possible to use heating model for ablation and collision mechanism for excitation. The whole process did not depend neither on gas pressure (vacuum 10^{-4} Pa or air) because of high pressure in plasma (10 MPa) nor on laser beam wavelength.

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M 27

STUDY OF FAST ENERGY TRANSFER IN BACTERIAL ANTENNAE BY MEANS OF HOLE BURNING SPECTROSCOPY

J. Pšenčík, M. Vácha, F. Adamec, M. Ambrož, J. Dian, J. Boček*
and J. Hála

Department of Chemical Physics, Faculty of Mathematics and
Physics, Charles University, Ke Karlovu 3, 121 16 Prague
*Department of Autotrophic Organisms, Institut of Microbiology
ČSAV, 379 81 Třebon, Czechoslovakia

The light harvesting and fast energy transfer from antennae to reaction centre are the first steps in the photosynthesis. Relaxation of the first excited electron singlet state and fast energy transfer to the reaction centre are connected with the homogeneous width of optical transitions. The spectral hole burning, time resolved and photon echo spectroscopy are independent methods enabling determination of the homogeneous widths from inhomogeneously broadened spectra.

The aim of this contribution is to present the results of low temperature (1.5-100 K) near infrared fluorescence and hole burning spectroscopy of photosynthetically active bacteria. Systematic studies of green photosynthetic bacteria *Chlorobium limicola* and *Chlorobium phaeobacteria* were performed on whole cells. The basic information about physical and chemical properties were obtained from absorption and fluorescence spectra. Architecture of light harvesting antennae containing chlorosomes and water soluble protein complexes is reflected in different energy transfer rate constants in comparison with purple photosynthetic bacteria without chlorosomes directly monitored by spectral widths of burnt holes.

M 28

MASS SPECTROMETRIC AND FT-IR IDENTIFICATION OF VOLATILE PRODUCTS OF RADIOLYSIS OF NITROBENZENE-CARBON TETRACHLORIDE-WATER TWO-PHASE SYSTEMS

Mihir K. Sahoo and J. Kuruc
Dept. of Nuclear Chemistry
Faculty of Natural Sciences, Comenius University
CS-842 15 Bratislava, C.S.F.R

Nitrobenzene-water and nitrobenzene-carbon tetrachloride-water two phase systems were prepared in different proportions of each constituent and then were subjected to ^{60}Co γ-irradiation to a dose of 197 kGy at a dose rate of 1.25 kGy hr^{-1} after a thorough shaking for five minutes. The organic phase of each sample was separated from the aqueous phase and were analysed by GC-FTIR-MS (capilary gas chromatograph HP 5890, series II; FT-IR spectrometer HP 5965 A; mass spectrometer HP 5971 A) method. Obtained spectras were analysed and compared with those in the data station to identify the various radiolytic volatile products were identified. Hexachloroethane, tetrachloroethylene, chlorobenzene, isomeric chloronitrobenzenes and isomeric dinitrobenzenes constitute some of the important radiolytic products.

M 29

INVESTIGATION OF ACTIVATED ZEOLITES BY DIFFUSE REFLECTANCE INFRARED SPECTROSCOPY

R. Salzer
Institut für Analytische Chemie
Technische Universität Dresden
Mommsenstr. 13, D-O-8027 Dresden

Infrared spectroscopy is considered to be one of the most sensitive methods in order to characterize activated samples under in-situ conditions. We have used diffuse reflectance infrared (DRIFT) spectroscopy to study the activation of powdered, undiluted zeolites. The experimental data were summarized in maps, which display the activation process quasi-continuously. Such contour plots can be generated for either a given sample or for a selected structural group among a series of related samples.

Investigations of activated samples are often injured by the presence of trace gases due to cell leakage. Leakage can be avoided by sealing the samples in glass tubes. It is shown, that such samples can be investigated in the mid infrared down to 2200 cm^{-1}. Very slow processes can be monitored even over months. We have studied the hydrogen spillover onto Y zeolites by DRIFT spectroscopy and by IR microscopy.

Raman spectra of activated zeolites and other activated samples are dominated by a strong background. We compare FT-NIR Raman and DRIFT data of glass covered activated H-erionites in order to identify the origin of the strong Raman background.

This work was supported by the "Fonds der Chemischen Industrie".

M 30

DETERMINATION OF ISOPROPYLIDENE GROUP ATTACHMENT SITE BY ^{1}H NMR

P. Sedmera,
Institute of Microbiolology, Czechoslovak Academy
of Sciences, Prague
K. Čapek,
Institute of Chemical Technology, Prague

The proposed method is based on the otherwise unresolved ^5J coupling between acetal methyl and OCH protons. At least one of the two methyls exhibits cross-peaks in delayed COSY spectra. As the same experiment also yields cross-peaks between the geminal methyls, full assignment can be completed by appropriate heteronuclear correlation. This approach was tested on 15 sugar derivatives of known or unambiguously determined structure having acetal rings of varying size attached at different positions.

M 31

MAGNETIC NONEQUIVALENCE OF A PHENYL GROUP: A CASE REPORT

P. Sedmera,
Institute of Microbiology,
Czechoslovak Academy of Sciences, Prague
J. Kuthan, and P. Šebek
Institute of Chemical Technology, Prague

Examination of three 6,7-benzo-1,3,5-triphenyl-4,8,8-trichlorobicyclo[3.2.1]octa-3,6-dienes by ^{1}H and ^{13}C NMR revealed a magnetic nonequivalence of protons and carbons of the phenyl ring attached to C-5. The phenomenon was studied by various 2D NMR techniques helped by fluorine labelling.

M 32

Sibilia C.
Universita "La Sapienza" di Roma, Dipertimento di Energetica
Roma

Abstract not delivered.

M 33

CHLOROPHYLL FLUORESCENCE OF CLONAL NORWAY SPRUCE MATERIAL UNDER DROUGHT AND OZONE STRESS

P. Smékal
Biophys. Dept., Faculty of Science, Univ. of Ostrava, Ostrava

Chlorophyll fluorescence reflects primary processes of photosynthesis such as light absorption, efficiency of photochemistry and energy transfer. The fluorescence induction kinetics key parameters were used for study of effect of drought and ozone stress on clonal spruce material.

It's namely known the environmental stresses that effect photosystem II cause a decrease of the F_v/F_m ratio and so in vivo fluorescence method is a rapid non-destructive method to study the physiological condition of plants to document stress effect and the regeneration of photosynthesis.

At the field station Klosterhede (Western Jutland, Denmark) there was used a forest stand with 40 years old Norway spruce trees selected for the establishment of four research plots (control, drought, irrigation and fertilization plot). Graftings of clonal Norway spruce material from old trees from respectively a western European provenance (Gludsted) and an eastern European provenance (Racovo) were received from the Arboretum at Hørsholm. The grafted shoots originated from 97 and 48 years old trees, respectively.

At the National Environmental Research Institute, Air Pollution Group at Risø (Denmark) there were used both beech samples (Fagus Sylvatica L.) and clonal Norway spruce material for the examination of physiological effect of ambient levels of ozone and slightly elevated ozone levels.

Fluorescence induction kinetics were measured with a field portable device PSM, BioMonitor S.C.I. AB Sweden suitable for outdoor measurement. The CPU was used for computation of fluorescence parameters (F_0, F_m, F_v, F_v/F_m, $t_{1/2}$) as well as for storage of the fluorescence induction curve.

M 34

THE USE OF DERIVATIVE SPECTROSCOPY FOR FOOD ADDITIVES ANALYSIS

Milan Suhaj

Food Research Institute,Priemyselná 4,Bratislava

The direct spectrophotometric methods used for food components analysis are characterized by errors caused by the interferences of the absorbing backround.These errors may be effectively eliminated by derivative spectrophotometry where the measured absorption spectra in digital form are mathematically transformed to derivative form using the algorithm by Sawitsky and Golay.The spectrophotometer Specord M 4C /Carl Zeiss Jena, Germany/ with computer casette Data Handling I was used for the formation of derivative spectra.

We have applied the method of derivative spectroscopy for some additives used in food manufacture.We have analysed:
acesulfame K-an alternative sweetener for soft drinks
saccharin-an alternative sweetener for different uses
quinine-taste modifier for tonic soft drinks
caffeine,theine-coffea and tea alcaloides used in some beverages
sorbic acid-food preserving agent
ascorbic acid-vitamin C .

In most cases,we have achieved very good recoveries and reproducibilities of analysis compared to other analytical methods,for example to capillary isothachophoresis.The method appears to be a perspective fast analytical method also suitable for determination and identification of other natural food components or additives,e.g. colorants and also contaminants.

M 35

ELECTRON PARAMAGNETIC RESONANCE OF HUMIC ACIDS

E.Šebestová,P.Stopka*,V.Machovič,H.Pavlíková
Institute of geotechnics,CSAS,Prague
*Institute of anorganic chemistry,CSAS,Prague

Humic material is organic matter of soil, lake and marine water sediments and peats. Humic acids are defined as hydroxide soluble part of humic material and consists of the polycondensed polyphenols with heterocyclic rings and functional groups containing N,S,O heteroatoms and short methylene bridges.

Humic acids play a very important role in the geochemical cycling and bioavailability of metals in sedimentary environment because of their ability to interact with metal ions. The nature of the bond between organic matter and metallic ions ranges from purely electrostatic such as metal adsorption or ion-erxchange reactions to covalent, as in the formation of hydroxo-complexes of chelate type. Most often cited model of metal chelation by humic acids is the salicylate type ring structure where metal is bonded through the carboxylic group on the humic polymer.

We studied the humic acids isolated by alkali extraction of subbituminous coals of North-western Bohemia. Paramagnetic metal complexes of coal derived humic acids from the seams Josef, Anežka and Antonín were characterised by the means of EPR spectroscopy. Complex of Fe(III) in rhombic coordination and organic radicals have been found in the spectra of all samples. In the spectra of the sample of humic acids from the coal seam Josef a high-spin Mn(II) and Fe_2O_3 were found. In the spectra of the other two samples vanadyl complexes were detected.

EPR spectroscopy gives us unique tool to distinquish between different forms and structural symetry of studied transition metal complexes.

M 36

FAST RELAXATIONS IN PHOTOSYNTHESIS STUDIED BY SPECTRAL HOLE BURNING

M. Vácha, F. Adamec, M. Ambrož, J. Dian, J. Pšenčik and J. Hála

Department of Chemical Physics, Faculty of Mathematics & Physics, Charles University, Ke Karlovu 3, 121 16 Prague, Czechoslovakia

Hole burning spectroscopy is a coherent laser spectroscopic technique that eliminates inhomogeneous broadening of optical spectra of guest molecules in solid matrices (e.g. chlorophylls in protein complexes at low temperatures) and enables to study directly the homogeneous spectral line profile. The homogeneous linewidth is proportional to the reciprocal total relaxation time of excited electronic states of the studied molecule. In the presence of fast energy transfer or charge separation the total relaxation time is predominantly determined by these processes. The high spectral resolution of hole burning technique offers an independent mehtod for the study of primary physical events in photosynthesis which include excited energy transfer in antenna light harvesting complexes and electron separation and transport in reaction centers. Both processes take place on the time scale of ps.

Here we present results obtained on photosynthetically active photosystem II particles as well as on isolated photosystem II antenna complexes. Persistent holes were burned in fluorescence spectra of a series of different inner and outer antennae. The holewidths extrapolated to zero burning fluence yield the excited energy transfer rates. The results enable to compare efficiencies of energy transfer within particular antenna units. Parameters of transient holes burned in fluorescence spectra of the electron primary donor of the photosystem II reaction center provide a complex picture of dynamics of the primary donor relaxation processes.

M 37

THE ANALYSIS OF WATER BY INFRARED SPECTROSCOPY

Z. Vavrouch, M. Pavonič
Water Research Institute, Brno

Infrared spectroscopy was used for the characterization and quantitative analysis of non polar extractable substances (oils) and also for the characterization of anionic and non ionic surfactans in polluted waters.

For the characterization of oil substances the extract of acidified water in the trichlorotrifluoroethane was used. In the IR silica region the analysis was performed by measuring the ratio of absorbances $R = A_{3030\ cm^{-1}}/A_{2930\ cm^{-1}}$ and degree of branching $R_{CH3/CH2}$ from particular absorbances $A_{2960\ cm^{-1}}$ and $A_{2930 cm^{-1}}$ after separating of polar substances.

For the characterization of oil substances the KBr region is also suitable by measuring the ratio of absorbances $A_{1600 cm^{-1}}/A_{1375 cm^{-1}}$, $A_{810 cm^{-1}}/A_{1375 cm^{-1}}$, $A_{810 cm^{-1}}/A_{720 cm^{-1}}$ and so on.

The quantitative analysis of non polar extractable oil substances was performed after the acidification of water and extraction with trichlorotrifluoroethane and separation of polar substances on silicagel. The stretching vibrations bands by 3030, 2960, and 2930 cm^{-1} were measured there.

The calculation of the oil concentration and using of different analytical standards are discussed.

Moreover anionic surfactans in water were characterized by IR spectra of their ionic associates with cationic dyes or their barium or calcium salts or complexes with p-toluidin hydrochloride but non ionic surfactans of polyoxyethylenic types by the spectra of complexes with tungstophosphoric acid or tetraphenylboronate.

M 38

THE IR STUDY OF K_2O-Fe_2O_3 SYSTEM.

E. Večerníková, F. Hanousek, V. Havlů *)

Institute of Inorganic Chemistry, Czechoslovak Academy of Sciences
256 67 Rez near Prague.
*) Research Institute of Synthetic Butadiene Rubber, Kralupy

We are presenting the infrared study of the system of K-ferrites, have been in the centre of interest over the last years as the catalyst for the dehydrogenation of ethylbenzene to styrene. A great problem in the literature are the controversy between the results of physical methods (esp. Moessbauer spectra or magnetochemical measurements) and actual structures of the compounds. We here compared the results from some physical or physicochemical methods, such as Moessbauer spectroscopy, X-ray diffraction, scanning electron microscopy, DTA and DTG methods vs. the results of IR spectra on the set of carefully prepared samples of the K_2O-Fe_2O_3 system and some commercial catalysts for the dehydrogenation of ethylbenzene to styrene (Shell, Girdler, Montedison, Cherox). The pure samples were prepared by combustion of the mixtures of K_2CO_3 and hydrothermally prepared α - Fe_2O_3 (hematite), γ- Fe_2O_3 (maghemite) or Fe_3O_4 (magnetite) in an electrical furnace at 800°C, with molar ratios K_2O / Fe_2O_3 varying from 0.08 to 1.0. From this comparison it is clear that IR spectroscopy is the most powerful method for identification of single phases, practically independent of the formation of solid solutions or nonstochiometric compounds. It can be concluded that only two compounds have a well defined structure, first the being the very unstable (sensitive to CO_2 or H_2O) simple cubic ferrite $KFeO_2$ (I) and the second, the most stable $K_2Fe_{12}O_{19}$ (II). The latter is the main phase identified in IR spectra of commercially prepared catalysts. Any other phases are only solid solutions of I and II or II and Fe_2O_3.

M 39

SURFACE ENHANCED RAMAN SCATTERING SPECTROSCOPY OF PORPHYRINS

B. Vlčková

Dept. of Physical and Macromolecular Chemistry, Charles University,
Hlavova 2030, CS 128 40 Prague 2, Czechoslovakia

Surface Enhanced Raman Scattering (SERS) spectroscopy is a progressive vibrational spectroscopic method based on 10^4 - 10^6 times enhancement of Raman scattering upon adsorption of the scattering species (e.g. porphyrin) on the roughened surface of Ag, Au or Cu. For porphyrins in general, an information about their interaction with metal surfaces as well as about their native, chemically unperturbed form is required by chemists. This survey demonstrates how both types of information can be obtained by SERS and SER*RS* (*R-resonance*) spectroscopy in systems with Ag colloid as active surface and TPPC4 (5,10,15,20-tetrakis(4-carboxyphenyl)porphyrin as a model porphyrin adsorbate.

Upon direct adsorption of TPPC4 on the surface of Ag colloid, the *Ag(II)TPPC4 surface complex* is formed [1]. The identity of the *Ag(II)TPPC4 surface complex* is proved by the full agreement of its SER(R)S spectrum with the SER(R)S spectrum of the Ag(II)TPPC4 complex syntesized. Moreover, systematic studies on the mechanism of the SERS active system formation show that direct adsortion of TPPC4 on the Ag colloidal surface is possible only owing to the high stabilization energy of porphyrin metalation. Obtaining the SERS spectrum of the native, free base form of TPPC4 in this system is thus virtually impossible.

Our results show that this drawback can be efficiently overcome by invention of a molecular spacer [2]. Molecular spacers have to possess two important characteristics:(1) the ability of spontaneous adsorption on the Ag colloidal surface upon formation of a SERS-active system and, (2) the capability of interaction with free base TPPC4 which results into the *Ag colloid/spacer/TPPC4* SERS-active system formation. In this system, the spacer plays a dual role: (1) attracts porphyrin molecules into the vicinity of the SERS-active surface while, simultaneously, (2) prevents their metalation by a chemical interaction with the surface. Two types of chemical species have, up to now, been proved to be efficient molecular spacers for free base TPPC4 : a non-ionic surfactant Triton X-100 and a series of lysin-containing polypeptides (e.g. polylysin, KA, KAA, KAAA; K-lysin, A-alanin, average degree of polymerization ca. 30). In both in the *Ag colloid/Triton X-100/TPPC4* and *Ag colloid/polypeptide/TPPC4* systems, the SER(R)S spectrum of the native, free base form of the porphyrin was obtained.

In conclusion, invention of a molecular spacer offers new possibilities for obtaining SERS-spectral information about the native form of an adsorbate not only for porphyrins, but for biomolecules in general.

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M 40

MOGADOC - A BIBLIOGRAPHIC NUMERICAL DATABASE FOR MOLECULAR SPECTROSCOPY AND MOLECULAR STRUCTURE

Jürgen Vogt
Sektion für Spektren- und Strukturdokumentation, Universität Ulm
Liststraße 3, W-7900 Ulm, Federal Republic of Germany

Molecular physical properties and structural parameters of gas-phase compounds are often published in sources, which are not well known, so that these data are easily overseen. Thus in order to facilitate the access to structural and related properties of free molecules, the Section for Spectra and Structure Documentation at the University of Ulm has compiled and critically evaluated for more than two decades literature in the field of high resolution spectroscopy (especially in the long wavelength region) and gas-phase electron diffraction.

This complete and worldwide unique compilation has been the basis to constitute the machine-readable database MOGADOC. This acronym stands for MOlecular GAs-phase DOCumentation. In connection with other inhouse database projects of Fachinformationszentrum Energie Physik Mathematik in Karlsruhe, the European host of STN International (The Scientific and Technical Information Network), a special database management system has been developed for IBM and IBM compatible personal computer under MS-DOS disk operating system. This inhouse database, which can be run locally by the Messenger retrieval language (widely used for STN International online databases), enables the user to trace back literature by means of bibliographic, physical and chemical search terms. As for the STN International online databases many interactive help facilities are accessible.

The MOGADOC database is a comprehensive machine-readable data compilation for gas-phase molecules, which have been investigated by microwave spectroscopy, radio astronomy and electron diffraction as well. It informs about spectroscopic, structural, dynamical, electric and magnetic properties of inorganic, organometallic and organic compounds. All information has been compiled mainly from scientific journals. Moreover the grey literature such as dissertation theses, reports and conference proceedings is also included. Hereby relevant abstracts from the Austin Symposia on Molecular Structure, the Ohio Symposia on Molecular Spectroscopy as well as from the European High Resolution Molecular Spectroscopy Conferences are taken into account. The literature is recorded back to

- 1930 for gas-phase electron diffraction
- 1945 for microwave spectroscopy
- 1960 for molecular radio astronomy

In total about 17,500 references (until 1991) are presently implemented for about 5500 compounds.

M 41

IR SPECTRAL ANALYSIS OF A MULTICOMPONENTAL MIXTURE OF HEPTANE AND HEPTENES BY KALMAN FILTER

K. Volka, M. Suchánek and P. Urban

Department of Analytical Chemistry
Institute of Chemical Technology
166 28 Praha 6, Czechoslovakia

The potential of the Kalman filter for analysis of a multicomponent mixture by infrared spectral analysis was tested. The object of the study was mixtures of heptane with heptene-1, cis-heptene-2 and heptene-3, which served as model of technologically interesting mixtures such as products of hydrogenation of oligomers. The minority components up to 5% contents were found to be determinable with a satisfactory accuracy and repeatibility.

M 42

IDENTIFICATION OF NATURAL DYES IN HISTORICAL TEXTILES

A. Kohoutová[a] , M. Novotná[a] a A. Samohýlová[b]

[a]Laboratory of Molecular Spectroscopy, Prague Institute of Chemical Technology, Prague

[b]National Conservator Studio, Prague

The Work is a contribution to the identification of natural textile dyes in unique gothic tapestries from the collection of the National Museum in Bratislava.

The dyes were extracted from the fibres and the evaporation residues were subjected to analysis by IR and UV-VIS spectroscopy.

A data bank of natural dyes used in the historical era concerned has been created and comprehensive IR and UV-VIS spectroscopic information requisite for their identification has been obtained.

INFRARED STUDY OF PROTON-EXCHANGED PLANAR WAVEGUIDES IN LITHIUM NIOBATE

M. Novotná [a], J.Hradilová [b] a J. Schröfel [c]

[a] Laboratory of Molecular Spectroscopy, Prague Institute of Chemical Technology, Prague

[b] Department of Inorganic Chemistry, Prague Institute of Chemical Technology, Prague

[c] Department of Microelectronics, Faculty of Electrical Engeneering, CTU, Prague

Lithium niobate is considered to be the leading electrooptical material for fabrication of active waveguides, modulators and switches for application in integrated optical circuits. These waveguides are fabricated in $LiNbO_3$ by Ti indiffusion and, more recently, by proton exchange.

In our report the Diffuse Reflection FT Infrared Spectroscopy in the OH-stretching and Nb-O fundamentals region has been used to determinate the extend of proton exchange in X-, Y- and Z-cuts lithium niobate, as well as the effect of subsequent annealing. The behaviour observed is consistent with the occurance of a diffusion-limited process within $LiNbO_3$. This measurements indicate that OH groups are substantially removed by annealing. From a combination of the results of infrared spestroscopy and optical waveguide measurements a mechanism of waveguide formation has been suggested.

M 44

FTIR ANALYSIS OF URANYL MINERALS

J. Vylita[a] , E, Janečková[b] a Z. Ksandr[a]

[a]Department of Analytical Chemistry,Institute of Chemical Technology, Prague

[b]Laboratory of Molecular Spectroscopy, Institute of Chemical Technology, Prague

IR spectra were measured for uranium minerals from the unique collection of the National Museum in Prague. Sample preparation techniques are described for the measurements in the absorption mode in KBr disks and in the diffuse reflectance mode. Comparison of spectra of the two kinds revealed that in some cases, of zippeites in particular, the KBr technique causes disturbances of the crystal lattice of the mineral and thereby distortion of the results. Some spectroscopic information is presented for classification of the minerals.

M 45

EPR OF Co^{2+} IONS IN $PbCl_2$ SINGLE CRYSTALS

J. Rosa[*], V.G. Gratschov[**]
[*]Institute of Physics, Czechoslovak Academy of Sciences, Prague
[**]Institute of Material Science Problems, Kiev

The X-band paramagnetic resonance measurements of Co^{2+} doped single crystals of $PbCl_2$ have been performed at helium-liquid temperatures. The EPR spectrum shows a remarkable angular variations of a rich hyperfine structure when two different octets of HFS can be distinquishet in selected orientations of crystalographic axes in static magnetic field.

It can be pointe out on the basis of these experimental facts that the spectrum commes from two electrically nonequivalent centres of Co^{2+} ions ($3d^7$, $S=1/2$) with very different parameters:

Co(I) : $g_x=5.07$; $g_y=6.01$; $g_z=1.956$; $\alpha=21°$; $A_x=282$; $A_y=400$; $A_z=75$;
Co(II): $g_x=4.00$; $g_y=6.25$; $g_z=2.820$; $\alpha=25°$; $A_x=156$; $A_y=330$; $A_z=56$;
(all A are in 10^{-4} cm^{-1} units)

of the effective Hamiltonian of the form:

$$\hat{\mathcal{H}} = \beta \hat{S}.g.H + \hat{S}.A.\hat{I} + \sum \hat{S}.A^i.\hat{I}^i \,.$$

SHFS with $A^i \sim 1mT$ can be observed only in the case of the centre II.
Different models of both centers are discused.

S 1

DETERMINATION OF STOPPING POWER OF ICE FOR FAST IONS BY RBS

P.Bauer[1], V. Nečas[2], W. Käferböck[1]

1) Johannes-Kepler-Universität Linz, A-4040 Linz Austria
2) Slovak Technical University Bratislava, CS-81219 Bratislava

The energy loss of a charged projectile while traversing a target material must often be known with great accuracy; this energy loss can either be measured directly or determined through calculation. At present various theories exist and each is valid over a specified interval of projectile velocity. Calculations of the stopping cross section for chemical compounds, which are based on the Bragg rule, are suitable as a first-order approach. However, this rule is not applicable at energies near the stopping power maximum [1], where the weakly bound valence electrons dominate the stopping process.

We have measured the stopping power of H_2O ice for protons, deuterons and alpha particles in energy range from 20 keV to 700 keV by means of Rutherford backscattering (RBS). The results are of fundamental interest for medical applications [2] and they are completing similar experiments with H_2O vapor [3].

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S 2

DETERMINATION OF MAJOR ELEMENTS IN SILVER ALLOYS BY THE LIQUID SAMPLE X-RAY SPECTROCHEMICAL METHOD

V.Budil
Safina s.p., Vestec u Prahy

XRF techniques was successfully used to analyse silver alloys from liquid samples. X-ray spectrometric analysis of solutions offers several advantages : homogeneity, ability to dilute matrix effects and ease of preparation of standards and samples. The measurements were performed with a PW 1404 sequential x-ray spectrometer equipped with a Mo side-window tube operated at 60 kV and 50 mA. A LiF 200 analyzing crystal, a fine collimator and a scintilation detector were used. Most samples of silver alloys can be easily prepared by dissolving 0.25 g sample in 25 ml weak nitrid acid.

Measurements were based on the use of incoherently scattered x-ray tube radiation to compensate for unknown and variable matrix effects due to metal ions and variable volume of solution in sample holders. A calibration curve was set up for each element using the de Jongh regression model incorporated in the Philips X44 software package. The reproducibility (RMS 1-sigma) was calculated and the value of RMS for all of the measured elements was significantly lower then 0.2 % for the concentration range from 0.1 to 100 %. The total measuring time for 4 elements (Ag, Cd, Cu, Zn) was 300 seconds. Owing to an optimal selection of spectrometer settings and sample preparation routines, the obtained accuracy and precision are corresponding with chemical methods. So we suggest this method as suitable for the precise and rapid analysis of major components of silver alloys.

S 3

MÖSSBAUER SPECTROSCOPY FOR SURFACE ANALYSIS

M.Carbucicchio
University of Parma, Department of Physic, Parma

Abstract not delivered.

S 4

EDX MICROANALYSIS OF AMORPHOUS BIMETAL INTERFACE

K. Csach, V. Ocelík, J. Miškuf

Institute of Experimental Physics, Slovak Academy
of Sciences, 043 53 Košice

The practical applications of amorphous metallic glasses are limited by thickness of ribbon in some cases. Perspective way to solve this problem is new technique based on preparation of layered structures by the modified planar flow casting method. Characterization of the interface between layers is an interesting question. Due to high cooling rate, which is necessary for obtaining amorphous structures, interface thickness is very small in comparison with spatial resolution of EDX microanalysis.

We have used bilayer ribbon with nominal chemical composition of the lower $Co_{67}Fe_4Cr_7Si_8B_{14}$ and of the upper $Fe_{40}Ni_{40}B_{20}$ layer, respectively (the samples were prepared by P. Duhaj in Institute of Physics SAS, Bratislava). Line scan data obtained in direction perpendicular to the ribbon surface were fitted by model curves.

Models were based on assumption that the distribution of generated x-rays in the direction perpendicular to the electron beam has two dimensional normal or exponential character or one dimensional exponential character.

One dimensional normal or exponential models of lateral distribution are suitable (with consideration of experimental error) for characterization of spatial resolution of x - ray microanalysis or for description of one dimensional change of the chemical composition perpendicular to the surface.

PYROLYSIS GAS CHROMATOGRAPHY - MASS SPECTROMETRY OF ACRYLIC DISPERSIONS

Z. Dušek, F. Herrmann

SYNPO s.p., Pardubice, Czechoslovakia

The present work shows the identification of major degradation products of polyalkylacrylates and methacrylates using pyrolysis gas chromatography - mass spectrometry.

Pyrolysis, or controlled thermal fragmentation, has been used for many years to elucidate organic structures. Pyrolysis gas chromatography (PyGC) was originally evolved to extend the separation capability and resolution of GC to the characterization of nonvolatile materials, such as polymers. In the following few years, however, PyGC has been applied to the analysis of many other materials such as paints, drugs, textiles, and even bacteria. The connection of gas chromatograph with mass spectrometer is necessary in this type of analysis.

The pyrolysis unit used for thermally degrading the polymer samples was a CDS 122 Pyroprobe (Chemical Data System, USA), consisting of a heated interface, platinium ribbon probe and electronic control modul. The interface was connected to the injection port of Varian Model 3700 Gas Chromatograph. For detection the low resolution quadrupole mass spectrometer Finnigan MAT 44S was used.

The major pyrolysis degradation products of acrylic homopolymers and simple copolymers was identified. Their mass spectra will be presented.

A COMPARISON OF THE THEORETICAL, EMPIRICAL AND EXPERIMENTAL APPROACH TO EVALUATIONS OF THE FUNCTION $\Phi(\rho z)$.

O. Gedeon, V. Hulinsky
Institute of Chemical Technology, Prague

All empirical approaches are blind in the sense that the physical background of their establishments is not clear and therefore it is very difficult and mostly impossible to develop them. From the theoretical point of view the best description of the electron penetration into the matter gives the one-electron Monte Carlo model due to elimination of the systematic errors according to the model used. In such a case the resulting error is given by the statistics apart from the precise evaluation of elemental processes. Elemental scatterings are based on the Rutherford elastic cross section, the "Bethe inelastic one" (it results from the transformation of the Bethe stopping power into the inelastic cross section.) and several types of the ionisation ones. Modeling is carried out for a few targets and calculated results are compared with the experimental as well as with the empirical curves of $\Phi(\rho z)$. The graphs obtained can serve as an sign-post which path should be followed on our way to the better analytical results: The empirical procedure combined with experiment or that one by means of which we obtain more and more precise evaluation of the elemental process and consequently more and more adequate description of electron penetration.

S 7

FIELD DESORPTION MASS SPECTROMETRY - AN EVALUATION

V. Havlicek
Institute of Microbiology, Prague

Field desorption (FD) was introduced in 1969 by H. D. Beckey and coworkers. It has become a frequently used method thanks to many advantages: high molecular ion yield, fairly high mass capability, applicability to a wide variety of compound types and availability on many general-purpose organic mass spectrometers.

The experimental procedure is not complicated. The sample is dissolved and deposited on an emitter, e.g. 10 um tungststen wire coated with carbon dendritic needles about 30 um in the length. This emitter mounted on a sliding pushrod probe is then introduced into the ion source via vacuum-lock and an acceleration voltage is applied to it. A slotted cathode mounted on equal rod and separated from the emitter by 2-3 mm is held at a potential 10-12 kV lower than that of the emitter. Established high field strengths present near the tips of the microneedles ($\sim 10^8$ V/cm) cause the disturbtion of the potential wall of the molecule so that an electron can "tunnel" (in the terms of the laws of quantum mechanics) from the molecule into unoccupied orbitals in the metal emitter. Formed positively charged ions of measured compound then desorb (using the direct or indirect heating of the emitter) and are accelerated into the mass analyzer.

However, FD has several disadvantages. The first is low sensitivity of the method, an order of magnitude or so smaller than that of EI, CI or FAB. Also FD sensitivity fluctuations may be observed. Another problem seems to be an ion current instability occuring especially with salts or other highly polar organics. These features together with considerable demand of experience are responsible for its lesser popularity among mass spectrometrists. Nevertheless, there are many cases where it is a method of choice.

S 8

THE STUDY OF INTERFACES IN B/Al COMPOSITE MATERIAL.

K. Iždinský, J. Ivan, A. Holý*

Ústav materiálov a mechaniky strojov SAV, Bratislava
*Výskumný ústav zváračský, Bratislava

Transmission electron microscopy and energy dispersive X - ray microanalysis have been applied to characterize the fibre-matrix interfaces in B/Al composite material. The B/Al composite material was prepared by hot press diffusion bonding of AlMg2 matrix monolayers reinforced with uniaxially aligned B fibres. The effect of thermal cycling and isothermal exposure on the properties of this material was studied then.

B/Al composite material keeps its properties practically up to the temperature of 673 K. Thermal treatment at 773 K, both isothermal and thermal cyclic results in a significant decrease of its mechanical properties. Mutual reaction between the matrix and the fibre was found as the reason for these changes. This reaction leads to the formation of interfacial reaction layer which results in the improvement of the interfacial bonding strength first and then in the decrease of the strength of fibres.

Ion milling was applied to prepare thin transmission electron microscopy samples. The fibre axes of the specimens were orientated parallel to the foil surface. Segregation of Mg (up to 37 %) at the interface was discovered. Three different borides - $(Mg,Al)B_2$; α-AlB_{12} and β-AlB_{12} were identified in the interfacial reaction zone.

S 9

MONITORING OF RADON AND OF ITS PROGENY

Čestmír Jech
Institute of Physical Chemistry and Electrochemistry,
Czech. Ac. of Sciences, Dolejškova 3, 180 00 Praha 8

Zdeněk Janout, Ján Koníček, Stanislav Pospíšil
Faculty of Nuclear Sciences and Physical Engineering,
CTU of Prague, Břehová 7, 115 19 Praha 1

Potential risk resulting from inhalation of radon can be assessed most directly by measuring air volume concentration of shortlived products of radon which are retained in the lungs during inhalation. The concentration of these products can be determined simply by passing a measured volume of air through a convenient filter and by **measuring the activity alpha deposited on the filter**, e.g. using silicon surface barrier (or PN junction silicon) detector. Through integrated counts over predetermined time intervals after collection, activity and thus volume concentrations of individual progeny members (which are generally not in a radioactive equilibrium) can be determined. More precise measurement and simple procedures are recommended and appropriate equations (which include pumping velocity, filtering efficiency, detection efficiency and the decay constants) solving this problem were derived. An alternative way to assess radon risk is the direct measurement of concentration of radon itself. This can be carried out very conveniently using an apparatus incorporating a chamber, from which the **charged radon decay products can be collected electrostatically** directly on the entrance window of a silicon detector placed into the chamber. The collection efficiency is dependent on humidity of the air in the chamber and generally only a fraction of the activity of the products can be collected.

Both types of measurements can be realised using a special hand-held PSDA (battery operated Portable Set for Detecting of Alpha activity) measuring instrument. With this apparatus the alpha activity collected in the filters can be measured using a built-in Si detector and sample holder. Alternatively the set provided with a built-in HV bias supply can be used to collect electrostatically the products from a large volume chamber (containing radon laden air) directly in the entrance window of the Si detector incorporated into the chamber. For the primary calibration of the chamber radon measurement a technique was devised which consists of: 1) implanting ^{222}Rn by recoil into a tin foil, 2) measuring its absolute activity and 3) releasing Rn by heat treatment into the chamber.

With the filtration method radon progeny concentrations down to about 10 Bq/m^3 are measurable with a relative 20% error. By means of electrostatic collection, radon concentrations can be measured with a 10 liter chamber in approximately the 500 Bq/m^3 range.

This work has been supported by the grant of CTU No. 8054.

S 10

EXPERIMENTAL VERIFICATION OF THE POUCHOU-PICHOIR METHOD FOR THIN FILMS ANALYSIS

K.Jurek,J.Chval,M.Šimecková
Institute of Physics CSAV,Praha

Electron microprobe analysis of thin films on substrates is still problematic inspite of many years effort of scientists in this field.The main reason is in accurate description of the electron scattering and X-ray generation not only in the thin film but also in the substrate.Contrary to the time consuming Monte-Carlo simulation of individual physical processes Pouchou and Pichoir method is based on empirical X-ray generation function represented by the combination of exponential and linear functions /1/. This function is determined by the material constants and energy of primary electrons and fitted by empirical parameters.

It was successfully used for ultralight elements analysis in homogenous bulk specimens /2/. However,such a unique function cannot describe the discontinuity on the interface film-substrate and can be only approximated by weighing of film and substrate parameters.If the film is very thin,the generation function can be described by the substrate parameters,while the thick layer approaches the bulk specimen. The intermediate case is most critical,especially if the atomic numbers of the film and substrate differ significantly.Therefore thorough testing is necessary.

Program Strata developed by Pouchou and Pichoir was used to calculate the dependence of k-ratio versus thickness of the film at several accelerating voltages and compared with experimental k-values and those calculated by Monte Carlo model /3/,/4/. Films of various thickness of Al and Au were deposited on substrates Si,Ni,and Pt for this purpose.Surprisingly good agreement of Strata calculations with experiments was obtained,much better than with Monte Carlo model (discussed in 4).

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FIM STUDY OF ELECTRONIC STATES AT INDIVIDUAL ATOMS ON TRANSITION METAL SURFACES.

Z. Knor
J. Heyrovský Institute of Physical Chemisty and Elektrochemistry, Czech Academy of Sciences, Prague

Invitation to the 9th Czechoslovak spectroscopic conference forced me to look for any connection between my non-spectroscopic activity and spectroscopy. This connection can be found in the visualization of symmetry properties of surface states of some transition metal atoms in the FIM (Field Ion Microscopy) experiments, since the symmetry (and energy) of electronic states belong to the corner stones of spectroscopic studies.

The usefulness of the concept of atomic-like states localised near the surface atoms has been demonstrated in the interpretation of the anisotropy of FIM images [1]. The field ionization has been qualitatively treated in terms of the formation of"quasichemical" surface complexes, resulting from the overlap between orbitals of the inert gas atoms and atomic-like orbitals of individual atoms on the metal surfaces (field adsorbed inert gas atoms [2]).This model can be exploited for the interpretation : i) of the triangular shape of FIM images of FCC, HCP and BCC individual metal atoms, residing on a flat (111) plane of a FCC metal and ii) of the changes of their orientation during hopping of these atoms between different types of adsorption sites on this plane.

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S 12

PIXE ANALYSES AT CZECH TECHNICAL UNIVERSITY IN PRAGUE

J. Král, V. Potoček, J. Voltr, R. Salomonovič

Faculty of Nuclear Science and Physical Engineering,
Czech Technical University, Prague

During the last decade equipment for the analyses with energetic light ions has been constructed and built up in the ion beam laboratory of the Dept. of Phys. Electronics, Faculty of Nuclear Science and Physical Engineering, CTU, using the ion beam from the 2.5 MeV Van de Graaff accelerator of Nuclear Centre, Charles University. Besides an experimental chamber the equipment has the analytical chamber with twenty position carousal, devoted to the analyses using Particle-Induced X-Ray Emission - PIXE. Recently, an improvement of the equipment has been performed to have external proton beam, allowing also analyses of samples which are not compatible with vacuum. Now, PIXE analyses may be conducted both in high vacuum and in an atmosphere with pressure lower than 10^5 Pa or even in open air. Proton beam with energy from about 0.6 MeV to less than 2.5 MeV and current from some tenths to about 100 nA is used. Its diameter is usually 6 mm in vacuum or 2 mm if the external beam is used, the nearly homogeneous part of broader beam being selected by a diaphragm. Otherwise, focused beam may be used with diameter about 1 mm in the target position. The unique feature of the equipment - vertical beam on the target - allows to analyze simply even liquid samples. At present, both routine analyses are performed, mainly of solid fraction of aerosols, and further development of the equipment and methodology for different kinds of samples takes place, to improve the effectiveness and the accuracy of the analyses. The main attention is devoted to the analyses of environmental samples.

S 13

3-DIMENSIONAL ELECTRON IMPACT MASS SPECTRA OF DIAZODIARYLMETHANES AND CYCLIC α-DIAZODIKETONES

J. Kuruc[a], E. Kardošová[a], L. L. Rodina[b], V. A. Nikolaev[b]

[a]Department of Nuclear Chemistry, Faculty of Science,
Comenius University, CS-84215 Bratislava, C.S.F.R.
[b]Department of Organic Chemistry, Faculty of Chemistry,
Sankt-Peterburg State University, RF-199034 Sankt-Peterburg,
Russian Federation

In this work we have measured the electron impact mass spectra of diazodiarylmethanes (diazodiphenylmethane, **Ia**; phenyl-*para*-methoxyphenyldiazomethane, **Ib**; phenyl-*para*--biphenyldiazomethane, **Ic**; 10-diazonaphthoquinone, **Id** and 9-diazothioxanthene, **Ie**) and cyclic α-diazodiketones (2-diazo-1,3-cyclohexanedione, **IIa**; 2-diazo-4,4-dimethyl--1,3-cyclohexane-dione **IIb**; 2-diazo-5,5-dimethyl-1,3-cyclohexanedione, **IIc**; 2-diazo-4,6-dioxa-5,5-dimethyl-1,3-cyclohexanedione, **IId**; and 2-diazo-5-phenyl-1,3-cyclohexanedione, **IIe**). The mass spectra were determined on a Varian MAT 111 instrument with a source temperature of 120 °C, ionizing electrons of 15-70 eV and 150 μA and sample reservoir laboratory temperature and presented as 3-dimensional mass spectra. In all the investigated diazocompounds, molecular ions with relatively small intensity (0.08-42 % of rel. abounds at 70 eV) were registered, which increases gradually with the reduction of energy of electrons. The dominant direction of fragmentation of these diazocompounds is primary elimination of N_2. Doubly-charged ions were observed in the mass spectra of diazodiarylmethanes. In mass spectra of **IIa-c,e** we observed the elimination of CO group after primary elimination $(M-N_2)$. This can be explained by the fact that after the elimination of N_2, α-ketoketenes are formed via Wolff rerarrangement. Molecule **IId** does not undergo Wolff rearrangement leading to the formation of α-ketoketenes, rather it is subjected to further fragmentation after the electron impact. For all investigated diazocompounds fragmentational schemes were proposed.

THE STUDY OF INDOOR AIR POLLUTANTS BY COMBINED GAS CHROMATOGRAPHY/ MASS SPECTROMETRY

S. Sollinger and K. Levsen, Fraunhofer-Institut für Toxikologie und Aerosolforschung,
Nikolai-Fuchs-Str. 1, D-3000 Hannover 61

While the contamination of the outdoor air as well as the occupational atmosphere has received considerable attention both by scientists and the public community, it has been overlooked for a long time, that the non-occupational indoor environment is polluted in particular by organic compounds which are often present in amounts, much higher than found outdoors. Except for some very toxic compounds like formaldehyde, polychlorinated dibenzodioxines and dibenzofuranes, asbestos and radon, the sources for these organic compounds is mainly unknown, as there are several indoor sources which release the same compounds, such as building materials, furniture, hobby activities and household cleaning. There is an increasing number of persons who complain about health affects, usually termed "Sick Building Syndrome".

The contamination of the indoor air by organic pollutants may considerably vary from home to home, and examples for this fact are presented.

The identification of sources for indoor contaminants is only possible by climate chamber studies. Such studies for emissions from textile floor coverings are presented. We use 0.03 - 1 m^3 climate chambers, the temperature, humidity and air exchange rates of which can be varied in large ranges. Sampling occurs by adsorption on Tenax TA and sometimes in addition on Carbosieve II. The compounds are thermally eluted into a combination of gaschromatograph/mass spectrometer by thermodesorption. This method leads to very low detection limits. In ten textile floor coverings 110 compounds could be identified until now, most of which could also be quantified. The dependence on the temperature, humidity, loading and air exchange has been studied in much detail. In most instances, identification of the compounds is not possible by gas chromatography alone, but necessitates the employment of combined gas chromatography/mass spectrometry (GC/MS), as apart from the usual solvents, there is a large variety of unexpected compounds emitted from textile floor coverings, which can be safely identified only by mass spectrometry.

S 15

INDUSTRIAL APPLICATION OF MÖSSBAUER SPECTROSCOPY

J. Lipka, J. Sitek, M. Hucl
Department of Nuclear Physics and Technology, Slovak Technical University, Bratislava

In the last decades Mössbauer spectroscopy (MS) has been intensively used in the applied research. Several physicists have found MS to be the best way of making particular measurements required in industrial processes. One of the best advantage from point of view industrial application of MS is the possibility to make analysis all iron containing materials.

The technology of iron pigments has been checked by MS. Detailed phase analysis of all iron components created during technological processes led to changes of technological conditions.

A yield of nickel from nickel-ore strongly dependes on oxi-reduction processes in the reducing furnace. The MS has been a useful tool to optimalize conditions of reduction and extraction of nickel from solution.

High quality steels for different part of nuclear power plant devices have been studied by MS. Phase analysis, temperature dependence of some steel properties, contents of retained austenite are main items of the Mössbauer measurements.

MS method was used to identify changes in surface, structural and spectroscopic properties of sulphides produced by mechanical activation.

Corrosion products formed in the different parts of nuclear power plants were identified. We have found that corrosion products are predominantly nonstoichiometric ferrous, cation deficient magnetite and lepidocrocite.

Some contribution we have done to estimation of the influence of the radiation charge for the steel proof samples from the pressure vessel of the V-213 power plant reactor.

Welding fumes from various types of welding processes were also investigated.

DO WE HAVE MARS SAMPLE ANALOGUES ON THE EARTH ?

J. Lipka, M. B. Madsen*, J. M. Knudsen*, S. Mørup**, I. Tóth
Department of Nuclear Physics and Technology, Slovak Technical University, Bratislava.
*) Physics Laboratory, H. C. Ørsted Institute, Copenhagen
**) Laboratory of Applied Physics, Technical University of Denmark, Lyngby

A conclusion from the Viking mission to Mars in 1976 was that the loose surface material of Mars contains a strongly magnetic minerals probably maghemite. Therefore terrestrial so called Mars sample analogues whose contain magnetic minerals are of importance for the preparation of the exploration of Mars.

There may be possibilities of performing *in situ* Mössbauer spectroscopy on Mars. To avoid the need for sample preparation the Mars Mössbauer spectrometer has to work in reflection geometry.

We have studied several categories of samples: impactites, rocks, basalts, soils and SNC meteorites those are believed to have arrieved on the Earth from Mars.

A large collection of impactites from different craters on the Earth contain iron mainly in the paramagnetic state. On the other hand impactites from the Monturaqui meteoric crater (Chile) seems to be very interesting. Therefore a piece of those impactites hase been studied in details using transmission and backscattering Mössbauer spectroscopy as a main tool.

Magnetite, maghemite, goethite and ferrous glass phase were identified. In a magnetic separate a bcc-structured iron-nickel alloy was found in addition to the oxide phases.

It has been shown that Mössbauer spectroscopy of ^{57}Fe in samples from Mars and from terrestrial Mars sample analogues may be a significant tool in understanding the red planet.

The comparison of the Mössbauer spectra measured *in situ* on the surface of Mars whith those obtained on the terrestrial samples could answer the question in the title of this contribution.

S 17

The PC-AT BASED MÖSSBUAER SPECTROMETER

M. Mašláň[1], D. Žák[1], V. Snášel[1], A.L. Cholmeckij[2], V.A. Evdokimov[2], O.V. Misevič[2], A.A. Fedorov[2], A.R. Lopatik[2]
[1] Palacky University, Olomouc, Czechoslovakia
[2] Byelorussian State University, Minsk, Byelorussia

The PC-AT based Mössbauer spectrometer is complete system for aquisition and simple analysis of Mössbauer data. The system consists of a PC-AT with 1 Mb RAM, double floppy disk drive, 40 Mb hard disk, laser printer, colour monitor with VGA graphic adapter, and data aquisition system, velocity generator, driving unit with mini velocity transducer, scintillation detector, high voltage power supply, single channel analyser, measure bench which have been made in our laboratories and ^{57}Co source in a Rh matrix.

Driving system uses a velocity transducer, which is equipped with $SmCo_5$ magnets. The sizes of the transducer are 60 mm lengthwise and 46 mm diameter, its weight is 450 g. Reference velocity signal is generated digitally. Velocity range is ∓ 30 mm/s, the linearity of driving system is better than 0.1 %. The constant acceleration and constant velocity modes can be used in Mössbauer measurements.

A scintillator $YAlO_3$(Ce) (thickness 0.5 mm) is used in the detector. Luminiscence maximum of this scintillator is about 350 nm, scintillation time is 28 ns.

Mössbauer spectra can be registrated in 1024, 512, 256 or 128 channels. The maximum input count rate is 10 MHz, the data capacity is $2^{24}-1$ counts/channel and dead time is 0.5 µs/channel. The experimental data are registrated by buffer memory of data aquisition system. The buffer memory communicates with computer processor by an interupt channel. Spectra are stored on hard disk, they can be display on the screen with 1024 horizontal by 768 vertical resolution and priting by the laser printer.

Software capabilities: Since normal programmes can run during data aquisition, the data aquisition system uses the main processor only when changing the parameters of the measurement and communicating the buffer memory with main processor. The software comprises programmes for display and priting of the spectra, a programme of experimental data filtration , a programme of Mössbauer spectrum curve fitting.

The measure bench is constructed for transmission Mössbauer measurements.

S 18

EDX ANALYSIS OF ORIENTED MAGNETITE AND SUPERCONDUCTIVE PARTICLES IN POLYMER

J. Miškuf, K. Csach, J. Ďurišin*, P. Kopčanský, I. Sargánková

Institute of Experimental Physics, Slovak Academy
of Sciences, 043 53 Košice
*Institute of Experimental Metallurgy, Slovak Academy
of Sciences, 040 01 Košice

The discovery of superconductive materials with critical temperatures above 90 K gives possibility of preparation new composite materials for basic research and nonconventional applications. From this point of view it is also interesting to study composition of magnetic fluids with superconductive particles.

For the experiment we have used high T_c- superconductive $Y_1Ba_2Cu_3O_{7-x}$ ceramic powders with about 3 μm size prepared by sol gel technique. These were inserted into water-based magnetic fluid with Fe_3O_4 very fine particles. This mixture was polymerized by vinylalcohol in magnetic field gradient. Obtained samples in foil form were examined by REM microscopy with EDX microanalysis. Superconductor and magnetite particles morphology and its size were characterized by REM and TEM microscopy, respectively.

Morphology and EDX analysis evaluate the lamellar structure of composite. Magnetite particles create fine lines according to the gradient of magnetic field. Superconductive particles aggregate in the similar shape, but with greater inter-line distances. EDX line scan analysis evaluated that all lines of superconductive particles always have neighbouring lines of magnetite particles.

ISOTOPIC EVIDENCE FOR THE EXISTENCE OF THE DIATOMIC SULPHUR MOLECULE WITH THREE POSOTIVE CHARGES

L. Morvay and I. Cornides
Physics Department, Faculty of Education, Nitra

In a search for triply charged small molecules we have identified two triatomic molecules (CS_2 and CSe_2) with three positive charges, and later we have shown that even the S_2 diatomic species may survive triple ionization.

In this research high accuracy mass measurement was used to identify the ionic species. Since the S_2^{3+} ion is the only triply charged diatomic molecule identified so far, we considered desirable to use stable isotope tracer technique as well to confirm its identification.

For this purpose two kinds of sulphure+graphite electrodes were prepared from sulphure of normal isotopic composition (95,02 % ^{32}S) and sulphure higly enriched in ^{34}S (92,1 % ^{34}S), respectively. The spectra were taken with identical sparking parameters, side by side on the same photoplate.

The evaluation of this experiment has shown that the line assigned to the $^{32}S_2^{3+}$ ions in the ^{32}S-spectrum (mass $21\frac{1}{3}$) was shifted to mass $22\frac{2}{3}$ in the ^{34}S-spectrum. The high accuracy mass measurements resulted in mass values of the ion $^{32}S_2^{3+}$ and $^{34}S_2^{3+}$ with the small errors of 0,000096 and 0,000074 0 and this error decreased to the negligible value of 0,000022 for the difference of the two masses (due to the elimination of all errors of common source).

S 20

MASS SPECTROMETRIC METHODS FOR ANALYTICAL AND ENVIRONMENTAL STUDIES

N.M.M. NIBBERING

Institute of Mass Spectrometry, University of Amsterdam,
Nieuwe Achtergracht 129, 1018 WS Amsterdam, The Netherlands

In the last decade the combination of mass spectrometry (MS) with the most commonly used separation techniques of gas-chromatography (GC) and liquid chromatography (LC) has become very sophisticated and therefore very powerful to identify and quantify volatile and non-volatile compounds at the picogram and nanogram level, respectively, in complex mixtures, such as environmental and biological samples.

This will be shown in the lecture in which first the capabilities of GC/high resolution electron impact and GC/multiphoton-laser ionization mass spectrometry for the analysis of volatile polyhalogenated and/or polyaromatic hydrocarbons in environmental samples will be discussed.

Subsequently the principles and merits of LC/MS interfaces for the analysis of non-volatile compounds in complex mixtures will be presented and exemplified.

Finally, examples will be given showing that in some cases without prior separation non-volatile compounds from complex samples can be analysed successfully by the application of field desorption and desorption chemical ionization/mass selected collision-induced dissociation mass spectrometry.

S 21

MOSSBAUER SPECTROSCOPY OF FROZEN SOLUTIONS OF SOME IRON COMPLEXES

S. Palágyi*+, Z. Homonnay**, A. Vértes**, T. Braun*

*Institute of Inorganic and Analytical Chemistry, Eötvös University
P.O. Box 123, H-1443 Budapest, Hungary
**Department of Nuclear Chemistry, Eötvös University,
P.O. Box 32, H-1518 Budapest, Hungary

The nature of the anionic $^{57}Fe^{III}$-halo-complexes and $^{57}Fe^{III}$-thiocyanate, as well as the cationic $^{57}Fe^{II}$-phenantroline complex in aqueous and organic solutions have been investigated. For Fe^{III} compounds, diethyl ether and for Fe^{II} complex, acetone, amyl alcohol and o-nitrobenzene were used as organic solvents. The spectra were recorded at 80 K and evaluated to obtain isomer shifts, quadrupole splittings and internal magnetic fields for different iron species.

The spectra show apparent differences in the nature of the anionic iron(III) complexes. The observations does not support the assumption that free tetrahedral iron(III)-tetrachloro-complex ions are present in all chloride containing systems, except water. In the etheric solutions most probably a six-coordinated complex is formed with two diethyl ether ligands. In the thiocyanate containing system, the difference between aqueous and etheric solutions is almost negligible and iron(III) thiocyanate species are present in both solvents. The spectra of Fe^{II}- phenantroline perchlorate system in tested aqueous and organic solvents exhibit no significant differences. This suggests that the nature of this cationic iron(II) complex is the same in both types of solvents.

+Present address: Institute of Radioecology and Applied Nuclear Techniques, P.O. Box A-41, CS-04061 Košice, Czechoslovakia

CYCLIC BORONATES IN MASS SPECTROMETRY OF ECDYSTEROIDS

J.Pis, T.Vaisar

Institute of Organic Chemistry and Biochemistry, Czechoslovak Academy of Sciences,
Flemingovo nam. 2, 166 10 Praha 6, CSFR

Ecdysteroids are polyhydroxylated steroid moulting hormones of insects. Because of structural complexity of their molecules NMR and mainly MS are most widely used for identification of their structure.

For mass spectrometric elucidation of structure of ecdysteroids various ionization techniques were used. The most usual electron impact ionization(EI) gives structural information from fragmentation at C17-C20 bond for ecdysteroids without C20,C22 diol system and C20-C22 bond for those with diol system present, however, there usually are only fragment ions from subsequent losses of molecules of water in high mass region and very weak or mostly no molecular ion in EI mass spectra. In desorption chemical ionization(DCI) both molecular weight information and fragmentation are obtained depending on the operation conditions. Fast atom bombardment(FAB) ionization gives abundant protonated molecular ion and only few fragment ions mainly from subsequent losses of molecule of water. Only in the mode of negative ions few structural characteristic ions were observed, however characteristic C20-C22 bond fission is not preserved for C20,C22 diolic ecdysteroids.

From cyclic boronates formed on C20,C22 diol system, presence of this can be inferred and from fragmentation pattern of the boronate the structure of both side chain and steroid nucleous can be deduced.

Reaction of before mentioned diol system with phenylboronic acid was used for derivatization of several free ecdysteroids, ecdysteroid acetates, acetonides and glycoside. This reaction can be performed on the FAB probe tip after measuring spectrum of non-derivatized sample and is completed in about three minutes resulting in formation of cyclic boronate on 20,22 diol system. This is reflected in mass spectrum by 86 mass units shift of protonized molecular ion. The rate of the reaction is much higher than that of possible competing reaction of reagent with glycerol which thus can be used as an matrix. This competing reaction becomes important in case of glycoside where secon boronate can be formed on the sugar. This problem can be overcome using 3-nitrobenzyl alcohol as an matrix with addition of water scavenger, i.e. dimethoxy propane. This way both mono- and diboronate adducts of 20-hydroxyecdysone 25-glucoside were observed.

However, the reaction can be reversed and cyclic boronate cleaved by addition of hydrogen peroxide again in few minutes. This reverse reaction was succesfully applied to analysis of crude extract of Rhaponticum carthamoides submitted to reaction with phenyl boronic acid before SPE. Solution from SPE containing boronates of 20,22 diolic ecdysteroids was sampled on the FAB probe tip and spectra of befor and after reaction with hydrogen peroxide were taken.

This excelent reaction previously used in HPLC and SPE was not only used for differentiation of isomeric ecdysteroids containing and not containing 20,22 diol system, but also for differentiation of isomeric ecdysteroids having 20,22 diol which differ in substitution of either steroid skeleton or side chain.

S 23

AIR QUALITY INVESTIGATION BY PIXE

V. Potoček, J. Voltr, J. Král, R. Salomonovič

Dept. of Physical Electronics, CTU (Faculty of Nuclear Science and Physical Engineering), Praha

PIXE (Particle-Induced X-Ray Emission) as an analytical method was first reported at 1970 from Lund, Sweden, and about ten years after the PIXE program has also been introduced in Czechoslovakia. The method is based on the spectral analysis of the characteristic X-rays emitted from the matter under its bombardment by energetic charged particles, in our case 1.5-2 MeV protons. It is fast, non-destructive, multielement and sensitive analytical tool which is almost ideal especially for an elemental analysis of aerosols and some types of biological samples. That is why the PIXE program was inspired with needs of the Institute of Landscape Ecology of the Czechoslovak Academy of Sciences in its beginning and why it is still directed to the application in environmental science.

The spectra of characteristic X-rays are processed by non-linear least-squares fitting to produce the intensities of separate spectral lines corrected for background, overlapping, pile-up effect and escape peaks. The routine can be used for all types of X-ray spectra, i.e. also in XRF and EMP. On the basis of its output data and tabled PIXE-relevant physical parameters, files containing the amounts of separate elements in nanograms per sample are generated for thin targets.

More then 500 samples were analyzed to calibrate the system, confirm the power of the new software and test some types of analytical methodologies, mainly those fitted to aerosol analysis for air pollution investigation. The PIXE analytical system has been proved to be ready for analyses for the purposes of environmental research with good quality. The mass limit for the statement of an element is 500 (Mn) to 2500 (Bi) ng/cm^2, i.e. 35-175 ng per sample with 3 mm diameter. The reproducibility is up to 10%, typically around 3-5%. Hundreds of samples per year can be analyzed non-destructively with average number of 15-20 elements detected.

As the examples of the PIXE application, the results of long term monitoring of aerosol in Praha and in the mount Kleť will be presented.

S 24

X-RAY SPECTROSCOPIC DIAGNOSTICS OF LASER-GENERATED PLASMA

O. Renner

Institute of Physics, Czechoslovak Academy of Sciences, Prague

Matter irradiated by intense laser beams rapidly ionizes and gives an origin to a plasma characterized by very high ion and electronic densities and by very high temperatures. In the past, the main interest in laser-generated plasmas (LPP) was directed towards inertially confined fusion (and possibly also weapon applications). Nowadays, an experimental research in this field is reserved just for several large facilities, however problems connected with laser plasmas as particle acceleration, generation of strong magnetic fields, the development and application of bright x-ray sources (including x-ray lasers) and others attract undiminished attention.

One of the most powerful techniques for studying laser-produced plasmas (and the only method which can provide an information on extremely hot and dense plasma) is x-ray spectroscopy. It is well known that high-temperature plasma produces intense emission in the soft and hard x-ray region. To understand a connection chain between this emission and the phenomena occurring in LPP, large hydrodynamics simulation codes such as LASNEX have been developed. However, even this strictly classified and time consuming code is not sufficient to calculate detailed x-ray spectra; to do this, the hydrodynamics is coupled with a full treatment of the ionization physics and radiation transport, as done e.g. by LLNL program package RATION. Under the assumption that the big code includes calculations of radiative losses pertaining to the energy balance of the system and that the detailed kinetics will not significantly alter this balance, the results of emission modeling can be compared with experimental data and significantly improve our knowledge on evolution and dynamics of LPP.

The basic measurement concepts, transient effects connected with high radiative fluxes and instrumental techniques of x-ray spectroscopic diagnostics applied to LPP are briefly reviewed, an optimum choice of the dispersive element and spectroscopic scheme is discussed from the point of view of desired spectral range, luminosity, dispersion, spatial, temporal and spectral resolution. Two methods of high-resolution spectroscopy (double crystal spectroscopy of pulsed sources and monochromatic imaging of LPP by spherically bent crystals) are described in detail, the results of interaction experiments at the laser system Perun (Institute of Physics) and Vulcan (Rutherford Appleton Laboratory) are presented.

S 25

MASS SPECTROMETRIC METHODS FOR DETERMINATION OF POLYCHLORINATED DIBENZODIOXINES AND DIBENZOFURANES (PCDD/F)

M.Ryska
Research Institute for Pharmacy and Biochemistry, Prague 3

PCDD/F have been subject of concern in the biomedical and environmental sciences because of their pronounced toxicological effects. Mass spectrometry has been the leading technique used in dioxin analysis ever since Baughman and Meselson in 1971 first reported its use for the quantification of 2,3,7,8-Tetrachlorodibenzodioxine (TCDD) by off line GC/HRMS in samples from South Vietnam that were contaminated after using so called "Agent Orange" in Vietnam war. A limit of detection at the low ppt level was achieved. Nowdays the EPA methods 8290 and 1613 are acknowledged routine analytical methods for the determination of PCDD/F at ppt or ppq levels in complex matrices. These methods are based on HRGC/HRMS analysis uring ^{13}C labeled compounds in isotope dilution technique after extensive chromatographic cleanup.

A critical review on other MS methods and their comparison with the EPA 8290 and 1613 is given. As the analytical results must concern at least 17 individual 2,3,7,8-chlorosubstituted congeners, the HRGC must be used. The high separative efficiency of HRGC cannot be substituted by any high selective nonseparative techniques. The LRMS (quadrupoles) cannot be an adequate technique for 2 reasons : 1) The sensitivity of quadrupole instruments is 1 to 2 orders of magnitude lower than the one of the sector instruments, 2) Even when using the HRGC, the high quantity of other chlorinated compounds present in samples e.g. PCBs, DDT, DDE, chlorinated xanthenes may interfere with PCDD/F. Alternative methods to HRMS in selectivity the MS/MS have been suggested, especially the hybrid MS/MS. Advantage of these alternative methods is discussed.

ROLL MAGNETIC ANISOTROPY STUDIED BY MEANS OF MÖSSBAUER EFFECT.

O. Schneeweiss, S. Havlíček
Institute of Physical Metallurgy, Czechoslovak Academy of Sciences, CS-61662 Brno, Czechoslovakia

Roll magnetic anisotropy describes a magnetic anisotropy induced by plastic deformation of ferromagnetic alloys. An elegant theory of this phenomenon presented by Chikazumi et al. [1] is based on formation of a directional order of like-atom pairs which is produced by movement of single dislocations during slip. Progress in the analysis of Mössbauer spectra enables to distinguish in spectra of deformed ferromagnetic alloys the part of specimen occupied by arrangements of high dislocations density (called as interfacial phase - IP) from the part of specimen in which the original crystalline structure remains with a relatively low dislocation density (called the crystalline phase - CP) [2]. The parameters of these components (phases) derived from the spectra allow us to bring a new view of the development of the roll magnetic anisotropy during cold rolling.

As examples we present investigation results of the deformation of Fe-12wt.% Si ribbons. From the spectra taken in transmission geometry for five different orientation of γ-beam and ribbon plane we have derived the contents of IP and CP, their magnetic splittings and isomer shifts and spin texture parameter R corresponding to the intensity ratios of the first and second lines in the Zeeman sextets as well. The results show that the IP plays an important role in the process of roll magnetic texture formation. This help to understand some features of roll magnetic anisotropy development which cannot be satisfactorily explained by the theory of Chikazumi et al.

[1] S. Chikazumi, K. Suzuki H. Iwata, J. Phys. Soc. Japan **15** (1960) 250.
[2] O. Schneeweiss, Materials Letters **11** (1991) 43.

S 27

MÖSSBAUER EFFECT ANALYSIS OF Fe-C PARTICLES PREPARED BY SPARK SYNTHESIS.

O. Schneeweiss, M. Kočová
Institute of Physical Metallurgy, Czechoslovak Academy of Sciences, CS-61662 Brno, Czechoslovakia

Mössbauer effect studies of materials composed of small crystallites bring important information about the structure and atomic configurations. Broad group of these materials are prepared by techniques of rapid quenching from plasma, gas or liquid phases. One of these methods is the spark erosion in many modifications, e.g., spark synthesis.

We have investigated Fe-C alloys prepared by spark synthesis. As electrodes pure Fe and pure C were used. The dielectric liquids were pentane and kerosene. The materials obtained have the form of powders with broad particle size distributions $\sim 0.05 \div 50\ \mu m$. The particles were divided into several parts according to either magnetic behaviour - ferromagnetic and nonferromagnetic - or according to the size. Mössbauer spectra were taken in transmission geometry using ^{57}Co in Cr as a source. The analysis of spectra was performed by standard method. Two main components were distinguished: (i) the crystalline one, having similar parameters as the corresponding bulk material and (ii) amorphous and interfaces represented by Gaussian distribution of a Lorentzian. The cementite dominates among the crystalline phases. The content of other phases (martensite and austenite) depends on quenching rate. The finest particles exhibit superparamagnetic behaviour. The parameters of the amorphous component correspond well with those published for the amorphous specimens Fe-C prepared by sputtering [1]. According to our results of phase analysis a description of the synthesis process during discharge and subsequent cooling will be proposed.

[1] G. Le Caër and E. Bauer-Grosse, Hyperfine Int. **47** (1989) 55.

S 28

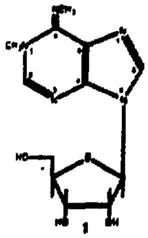
MASS SPECTROMETRY OF URINARY NUCLEOSIDES : POTENTIAL MARKERS OF AIDS AND CANCER

Karl H. Schram
College of Pharmacy, University of Arizona, Tuscon, AZ 85721 USA

The identification and quantitation of nucleic acid bases and nucleosides in normal and pathogenic human urine is of considerable interest because elevated, or depressed, levels of these compounds have potential utility as "biological markers" of cancer[1] and AIDS[2]. Thus, over the past 15 years, the levels of modified nucleosides in cancer patient urine have been monitored in an effort to develop methods for 1) the early detection of cancer; 2) following the patients response to therapy; and 3) detecting relapse prior to the appearance of clinical signs of recurrent disease.

Analysis of tRNA from various species has led to the identification of more than 40 modified nucleosides[3], some of which have been identified in human urine, while approximately 10 "non-RNA" modified nucleosides have been identified[1] in normal and cancer patient urine.

Methods for the isolation of the nucleosides from human urine and the subsequent identification of novel nucleosides in human urine using GC/MS techniques will be illustrated using examples of nucleosides recently discovered in the authors laboratory, e.g. N1, N^6-dimethyladenosine (1)[4] and 5'-deoxy-5'-methylthioguanosine (2).[5]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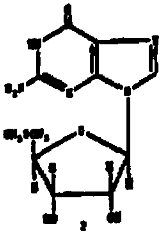
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The potential clinical significance of modified nucleosides in the urine of cancer and AIDS patient urine will be described.

S 29

PHASE ANALYSIS OF NANOCRYSTALS

J. Sitek and I. Tóth
Department of Nuclear Physics and Technology, Slovak Technical University, Bratislava

Amorphous ribbons of composition $Fe_{73.5}Cu_1Nb_3Si_{13.5}B_9$ have been annealed above their crystallization temperature which produces a homogenous ultrafine structure of alfa-FeSi with typical grain diameters of 10-20 nm. The formation of this nanocrystaline structure is ascribed to the addition of Cu and Nb. The experimental results showed that the annealed samples also consisted of residual amorphous phase in wide temperature range. Two samples of different thicknesses 33 µm and 27 µm were isothermaly annealed at the temperature 818 K from 0,5 to 5 hours in vacuum furnace. The amount of the crystalline phase increases rapidly in thicker sample. Both samples contained small amount of residual amorphous phase even after 5 hours annealing. The crystalline part of Mössbauer spectrum consisted from four sharp sextets attributed to DO_3-FeSi alloy but one cannot rule out other elements in the alloy. The total crystallisation occours at the temperature 923 K. After this temperature amorphous phase was not observed and the crystalline phase consisted of DO_3-FeSi alloy, $Fe_{24}B_6$ compound and presumably FeNbB alloy.

S 30

METHODS FOR DETERMINATION OF MnO_2 AND MnO IN MANGANESE ORES AND FeO IN IRON ORES AND SINTERS USING X-RAY FLUORESCENCE ANALYSIS

Grażyna Stankiewicz[x],Vaclav Helan[xx],Bohumila Svardalova[xxx]
x Institute for Ferrous Metallurgy,Gliwice,Poland
xx Trinec Iron and Steelworks,Trinec,Czechoslovakia
xxx Research Institute of NH,Ostrava,Czechoslovakia

An x-ray fluorescence method for the analysis of manganese ores , iron ores and sinters has been applied .
The possibility of application of the $K\alpha$, $K\beta$ and low energy satellites ($K\beta'$) spectral lines to quantitative determination of manganese and iron in various oxidation states by XRFA was also detailed studied .
The chemical shift of the $K\beta_{1,3}$ line of manganese and iron and the shape of the $K\beta_{1,3}$ - $K\beta'$ profile have been investigated . It was established , that the chemical shift of the $K\beta_{1,3}$ line as well as the $K\beta_{1,3}$ - $K\beta'$ peak profile varies in a characteristic way with the valence of manganese or iron .They can be used to determine the average valence of manganese or iron , and after that for quantitative determination of the MnO_2 , MnO and FeO in examined materials .
An investigation was also made of the peak intensity ratios $K\beta'/K\beta$ for manganese and $K\beta/K\alpha$ for iron in different "average" oxidation states of Fe and Mn atoms existing in ores and sinters .
The relationship between these peak intensity ratios and average valence of manganese or iron was established .
The $K\beta/K\alpha$ intensity ratio can be used to quantitative determine relative FeO and Fe_2O_3 contents with respect to the total iron content ($Fe_T \cong Fe^{2+} + Fe^{3+}$) and the $K\beta'/K\beta$ intensity ratio can be used to quantitative determine relative MnO_2 and MnO contents with respect to the total manganese content ($Mn_T \cong Mn^{4+} + Mn^{2+}$) .
The accuracy of the XRF determinations of MnO_2 , MnO and FeO is comparable with accuracy of wet chemical analysis this compounds .

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DETERMINATION OF CARBON AND NITROGEN IN STEELS BY ELECTRON MICROANALYSIS

J.Vřešťál*, B.Million, J.Pavlovský, Institute of
Physical Metallurgy, Czech.Acad.Sci, Brno,
K.Stránský, A.Rek, VÚ 070, Brno
*present address Inst.Phys.Chem.,Fak.Sci.Masaryk
Univ.Brno

The paper deals with two problems: the determination of the detectability limit of carbon and nitrogen by the energy dispersive X-ray microanalysis and the determination of total carbon concentration in ferrite-cementite steels with coarse cementite particles by the wave dispersive X-ray microanalysis.

The detectability limits of C and N were tested by means of energy analyser Kevex Delta V. in connection with the electron microprobe JXA - 8600.

The following detectability limits were found:

for carbon:c(min)= 1.59 wt.%, and for nitrogen:c(min)= 0.261 wt.%.

The mean deviation of single measurement at the detectability limit is approximately equal to s = c(min) / 2.

The energy dispersive analysis may be succesfuly used for qualitative analysis of carbon, and for quantitative analysis of nitrogen.

The new method for determination of the total carbon concentration in ferrite-cementite steels with coarse carbide particles was developed. The method is based on the dissolution of carbide particles by rapid heating followed by quenching.

The line analysis is done by the scaninng electron microscope SEM-505 Philips with the wave dispersive analyser Microspec WDX-2A. The measured CKa radiation on sample is compared with the measured CKa radiation on standards of iron with various carbon content. The standards containing homogeneously distributed carbon in iron were prepared by induction heating and centrifugal casting. It has been prooved that the carbon content measured represents well the total concentration of carbon in steel. The detectability limit is c(min)= 0.03 wt.% in this case.

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Attenuation of electrons in electron spectroscopy: analytical expression of elastic scattering processes.

W.S.M. Werner

Institut f. Allgemeine Physik,
Technical University Vienna
Wiedner Hauptstr. 8–10, A1040 Vienna, Austria.

Abstract.

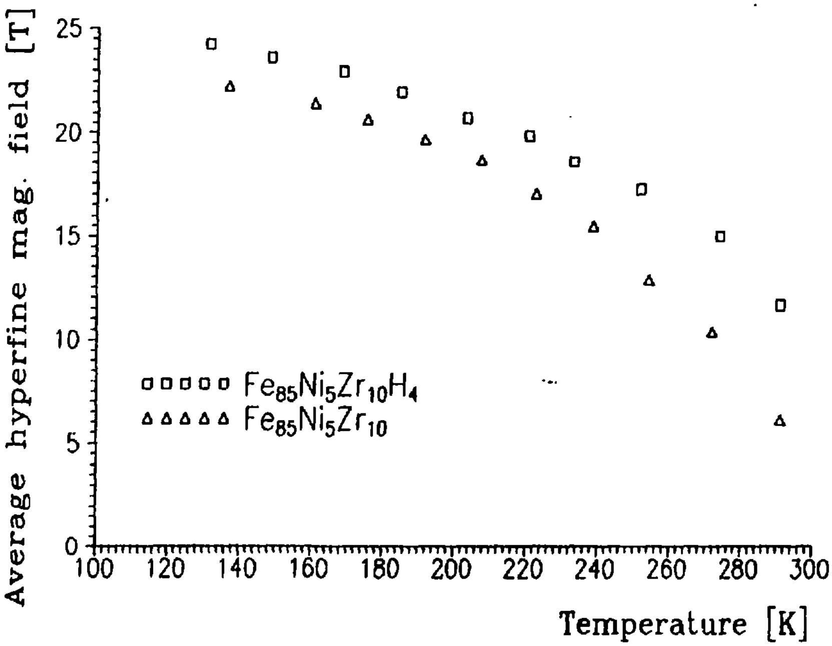
The study of electron attenuation in solids, as relevant for electron spectroscopy, has focussed on the effects of elastic scattering recently. In a large number of works the importance of this effect has been realized and emphasized, and in a number of recent works an empirical an alytical depth distribution function (DDF) has been derived. This DDF is intended to provide a quantitative description of the surface sensitivity of the electron spectroscopy and therefore plays a very important role in quantitative and angle resolved electron spectroscopy. In the present work, a detailed outline of the formalism and physical processes connected with this DDF is presented. A quantitative comparison of the present formalism with results from Monte Carlo calculations found in the literature yields very satisfactory results. At present, transport theory gives only qualitative results concerning some of the essential features of the DDF. These are in very good agreement with the empirical DDF and with Monte Carlo results. A few examples of applications of the formalism are presented. These comprise the determination of escape depths and the angular resolved electron spectroscopy. Excellent results are obtained. The results suggest that, as far as the effects of elastic scattering are concerned, the attenuation parameter (AP), which assumes a central role in the formalism, has an unambigous definition, and can be calculated analytically, can be used instead of quantities like the attenuation length, escape depth and the like.

HYDROGEN INDUCED CHANGES IN THE HYPERFINE MAGNETIC FIELD OF AMORPHOUS Fe-Ni-Zr ALLOYS

M. Zatroch, P. Petrovič, I. Brovko, M. Konč, T. Švec

Dept. of Experimental Physics P.J.Šafárik University, Košice

Mössbauer spectra of as prepared and hydrogenated amorphous $Fe_{90-x}Ni_xZr_{10}$ (x=0,2,5) alloys have been recorded at different temperatures. The samples were prepared by melt spun and hydrogenated electrolytically in 0.5M solution of H_2SO_4 containing a few ppm. CS_2. The hydrogen content was determined by measuring the pressure of gas evolved on heating.



Hydrogenation increases both the Curie temperature and the average hyperfine magnetic field. We purpose the volume effect plays the significant role in this, because hydrogen increases Fe-Fe interatomic distances. Hydrogen promoted changes decreases with Ni concentration.

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NONDESTRUCTIVE CONCENTRATION DEPTH PROFILES OF INDIUM PHOSPHIDE NEAR SURFACE REGIONS

J. Zemek
Institute of Physics, Czechoslovak Academy of Sciences, Prague

Sputtering of solid surfaces with rare gas ions in combination with surface sensitive techniques is extensively used to produce clean surfaces as well as to obtain depth composition information with high spatial resolution normal to the surface. Sputtering, however, frequently damages the surface structure and alters the near surface composition and chemical bonding.

An evaluation of the angular-resolved (AR) photoelectron spectra, which offers a nondestructive layer-by-layer analysis of near surface region within an information depth (~2-8 nm), can contribute to obtain more reliable data. The method is based on a modification of an information depth (ID). The ID is approx. $3\lambda \cos \theta$. λ is the inelastic mean free path of photoelectrons and θ is the photoelectron take-off angle with respect to the sample normal.

Considering a quantitative level of the depth distribution of atoms, several methods have recently been developed. A common feature of the methods is a dissertion of the near surface region of the sample into parallel layers and an evaluation of individual layer contributions to the net photoelectron line intensity. The AR photoelectron intensity conversion into the concentration depth distribution belongs to a class of ill-posed problems characterized with high sensitivity to experimental data errors and to solve it unconventional computational algorithms are required.

One of the most sophisticated procedure [1] is based on the regularization theory with inclusion of a priori information about the solution: the desired function of dependence between concentration and depth should be (i) non-negative, bounded and (ii) should not have more than one extremum up to the ID. The formalism has been tested on simulated data as well as using simple structures as a thin Ag film on Al_2O_3 or SiO_2 on Si.

In this contribution some benefits and limitations of the method are briefly discussed. Several applications of the method to the concentration depth profile of native oxide grown on InP and to study the altered layer composition are mentioned, taking into account corrections for elastic scattering and analyzer acceptance angle finiteness.

[1] O. A. Baschenko and V. I. Nefedov, J. Electron Spectrosc. Relat. Phenom. 53, 1 (1990).

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MASS SPECTRAL ANALYSIS OF PHOSPHOLIPIDS IN HUMAN CEREBROSPINAL FLUID

P. Miketova[1,2], N. N. Mollova[1,2], I. M. Moore[2] and K. H. Schram[1]
Colleges of [1]Pharmacy and [2]Nursing, University of Arizona,
Tucson, AZ 85721

Phospholipids are one of the main classes of lipids in the cell membranes of living organisms. Their low volatility and thermal lability have created difficulties in the application of mass spectrometry for their structure elucidation. The resurgence of interest in mass spectrometry of phospholipids is due primarily to the development of fast atom bombardment (FAB) ionization which allows the nonvolatile phopholipids to be analyzed without prior derivatization. Phospholipid research has recently centered around the use of phospholipids as biomarkers for bacteria and algae, and the determination of general membrane function in living matter. Our interest in phospholipids stems from their potential usefulness as biomarkers for the detection of the early membrane damage of the central nervous system following treatment with whole brain radiation and intrathecal chemotherapy in children with acute lymphoblastic leukemia and brain tumors.

The characterization of phospholipid content of cerebrospinal fluid (CSF) during the treatment could enable us to find a marker for the central nervous system tissue damage. The major membrane phospholipids found in normal human CSF include: phosphtidylcholine (PC), lysophosphatidylcholine (LPC), sphingomyelin (SM), phosphatidylethanolamine (PE).

In the positive ion FAB mode, the major fragmentation is cleavage of phosphate/glycerol bond, resulting in a loss of the polar head group. PC, LPC and SM fragment so that the choline head group usually retains the charge giving ion of m/z 184. This fragment is used for characterization of these three classes of phospholipids. PC, LPC and SM give intense peaks for MH^+, which is useful for their identification in the CSF total lipid extract. For better characterization of the molecular species HPLC separation prior to the FABMS analysis may be needed.

In the case of PE and PI the polar head group is lost as neutral, while the rest of the ion retains the charge. The relatively low intensity MH^+ signals for PE and PI make their detection in mixtures difficult by conventional FABMS. In this case a previous HPLC separation of the lipid mixture is necessary for their characterization.

The spectra of the total lipid extracts show that FABMS is method of choice for lipid characterization of CSF. On the other hand, these results demonstrate the potential usefulness of FABMS for following the chemotherapy and radiation treatment of children with acute limphoblastic leukemia and brain tumors.

MÖSSBAUER SPECTROSCOPY FOR SURFACE ANALYSIS

M. Carbucicchio
Department of Physics, University of Parma, Parma, Italy

Essentially, a Mössbauer spectroscopy experiment consists in measuring the resonant excitation of nuclear states, by means of *recoil-free* γ-rays emitted by a radioactive source. Most experiments are carried out in trasmission geometry, where a decrease in the γ-rays passing through the sample makes it possible to detect the resonant excitation.

An alternative approach consists in detecting, in scattering geometry, the photons or electrons emitted by Mössbauer atoms, after the resonant absorption, as a consequence of the decay of nuclear spin states. Depending on the kind and energy of detected radiation, Mössbauer spectra can be obtained for surface regions of different depths.

In the present work the principles and applications of electron Mössbauer spectroscopy (EMS) are reviewed in detail. Consideration is given to the surface selectivity and sensitivity of EMS, and experimental and theoretical aspects of the method are discussed.

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